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ERRATA.

Page 63 line 3, *for* malic acid *read* aspartic acid.
    ,, 63 ,, 22, *for* service-tree *read* mountain-ash.
    ,, 66 ,, 14, *for* service-tree *read* mountain-ash.
    ,, 68 ,, 4 from bottom, *for* iodine *read* iodide.
    ,, 101 ,, 14, *for* c is common to the zones *eb, va, read a* is common, &c.
    ,, 102 ,, 17, *for* all *read* also.

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I.—*On the Decomposition of Citrate of Lime in contact with putrefying Curd.*

By HENRY HOW, ESQ.

ASSISTANT TO DR. THOS. ANDERSON OF EDINBURGH.

The following notes are intended as a contribution to the knowledge already existing of the decompositions produced in complex organic molecules by contact of fermenting substances. Although in the present instance the study of the subject is incomplete, for reasons to be specified, I thought the few facts in my possession sufficiently interesting to be made known in the mean time, as a number of experiments of the nature to be described, sufficient for supplying the whole of the information sought, will possibly occupy a very long period.

The subject of the peculiar action set up in bodies by contact of ferments and putrescents has proved very interesting, and, in the case of the organic acids, the results as yet obtained present considerable uniformity. From experiments of this nature made with some of the vegetable acids, and acids derived from them, we see succinic acid occurring as an almost constant product, accompanied in some instances by one or other of the acids $C_n H_n O_4$. Thus Dessaignes[*] has shown that malate of lime yields succinic acid, and Liebig[†] that acetic and sometimes butyric acid occur in the same process, the formation of either of these volatile acids depending on the relative proportion of ferment and salt employed. The former chemist has

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[*] Compt. Rend. XXVIII, 16.   [†] Ann. Ch. Pharm. LXX, 104.

further shown* that fumaric, maleic, and aconitic acids all yield succinic acid under the same circumstances; but he does not mention whether he observed the formation of volatile acids. He remarks, however, that citrate of lime and citrate of soda afford no succinic acid.

Tartrate of lime was submitted to a similar trial some few years ago by Nölluer.† He suffered this salt, as prepared from crude tartar, to undergo spontaneous fermentation, and he obtained a volatile product which he termed *pseudo-acetic acid.*

Consideration of the foregoing facts, induced me to examine more particularly the change produced upon citric acid by contact with a putrescent body.

The experiments I am about to detail were performed in Dr. Anderson's laboratory, in Edinburgh.

Some crystallized commercial citric acid was powdered up with an excess of chalk and some water to a thin paste. When effervescence had ceased, dried curd to the amount of a fourth part of the acid employed was beaten up with the mixture, which was then transferred, along with about ten times its bulk of water, to a glass flask. This was furnished with a gas-evolution tube, and placed in a warm situation, where a thermometer immersed in the mixture indicated a temperature varying between 80° and 100° Fah. The whole began to stink in three days, and in about ten days fermentation seemed at its height; the gases evolved were carbonic acid and hydrogen, and at this period the former stood to the latter in the ratio of two volumes to one; the quantity of gaseous product afterwards decreased, and the relative proportions of the individual gases changed, the hydrogen preponderating. Of the last portions of gas collected about three volumes in four were hydrogen. The process was stopped on the twenty-second day, when a large amount of lime was found to be in solution, while a slimy sediment remained at the bottom of the flask, containing the undecomposed curd, and the excess of chalk. I could detect no succinic acid.

The fluid was filtered off, and precipitated by carbonate of soda; the filtrate from the carbonate of lime was evaporated to a very small bulk; the syrupy fluid on being allowed to cool, became a nearly solid mass, without exhibiting any distinct signs of crystallization. It was diluted with water and distilled with an excess of sulphuric acid, the products being carefully condensed in a Liebig's apparatus The fluid which passed over had a strong acid reaction, and smelt of a *fatty* acid; the distillation was continued till about half of the

contents of the flask had evaporated. The product was received. in three separate portions: the first, on the commencement of the distillation, showed a slight opalescence, apparently caused by the presence of an oily substance, possibly a little "ferment oil;" this, however, soon disappeared, and the whole of the fluids collected were clear and homogeneous.

A silver-salt was made from the first portion by neutralizing as nearly as possible with ammonia, and addition of nitrate of silver. A copious white flocky precipitate fell; it was collected and washed with cold water. On attempting to re-crystallize it from boiling water, it was found that while the greater part dissolved, considerable colouration took place, and a small portion remained black and undissolved. The filtered fluid was not completely colourless; however, it deposited a salt in white rounded granules, which, under strong magnifying power, presented a peculiar appearance, resembling the form of sasifrage or lycopodium. It was found to withstand the action of light, remaining perfectly white after some days' exposure, but was speedily blackened at a temperature of 212° Fah.; it was therefore dried in vacuo for analysis:

$$\text{I. } 5 \cdot 402 \text{ grains gave:}$$
$$3 \cdot 295 \quad \text{,,} \quad \text{carbonic acid, and}$$
$$1 \cdot 175 \quad \text{,,} \quad \text{water,}$$
$$4 \cdot 278 \quad \text{,,} \quad \text{gave, on ignition,}$$
$$2 \cdot 675 \quad \text{,,} \quad \text{metallic silver.}$$

A second salt was made from the same portion of the distillate in the same manner, but it was not recrystallized; of this,

$$\text{II. } 5 \cdot 800 \text{ grains, died in vacuo, gave on ignition}$$
$$3 \cdot 578 \quad \text{,,} \quad \text{silver.}$$

	I.	II.	Mean.			
Carbon	16·63			17·23	C_5	30
Hydrogen	2·51			2·29	H_4	4
Oxygen				18·39	O_4	32
Silver	62·52	61·68	62·10	62·09	Ag	108·1
	100·00	100·00	100·00	100·00		174·1

Although the above results differ somewhat from the theory given, the discrepancy is not remarkable when the decomposible nature of the salt is taken into account; and this allowance being made, the constitution of the salt is most simply represented by the formula,

$$\text{AgO} \cdot C_5 H_4 O_3.$$
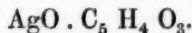
Interested by this apparently anomalous formula, I endeavoured to obtain the acid *per se*, by forming in the first place its lead-salt, and then distilling with strong sulphuric acid.   For this purpose, I saturated as nearly as possible the remainder of the first portion of the distillate with carbonate of lead, and evaporated the fluid so obtained to a very small bulk in the water-bath; a syrup remained, which after a considerable time became an opaque and crystalline solid mass.   A portion of this was found continually to lose weight by protracted heating at 212°, the acid apparently going off.   The remainder of it was distilled with strong sulphuric acid; a pungent acid liquor was obtained, but its quantity was too small to admit of any experiments to determine its boiling-point, &c.; it was therefore saturated with carbonate of soda, and nitrate of silver was added to the solution; a salt was obtained agreeing closely in its external characters with that already described; it was analysed:

6·167 grains, dried in vacuo, gave :
3·855   „   carbonic acid, and
1·435   „   water,
4·483   „   dried in vacuo, gave, on ignition,
2·802   „   silver.

The percentage calculation from these numbers gives a close approximation to those before obtained:

	Found.	Theory.
Carbon	17·07	17·23
Hydrogen	2·58	2·29
Oxygen	17·85	18·39
Silver	62·50	62·09
	100·00	100·00

and these results show that, whatever may be the nature of the acid, it remains unchanged during the whole of the processes above-mentioned.

As before remarked, the most simple formula expressive of the constitution of the silver-salt, is

$$AgO \cdot C_5 H_4 O_3;$$
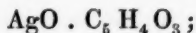
this is, however, an improbable constitution, and the formula requires to be doubled to assume a more reasonable character; if this be done, we obtain

$$2 \, AgO \cdot C_{10} H_8 O_6,$$
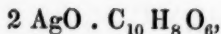
which would be the representation of a neutral salt of a bibasic acid,

$$C_{10} H_{10} O_8.$$
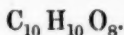
Such a substance has not as yet been met with in an isolated state ; but two salts are described,* which undoubtedly contain the elements in proportions corresponding to such a formula, and the method of their formation indicates clearly the nature of the acid in question. They are produced by mixing together salts of acetic and of propionic acids ; the first is a soda-, the other a silver-salt, which last agrees in such of its characters as are described, with those mentioned above, excepting perhaps the slight difference that its crystals are described as dendritic. I consider, therefore, this acid to be what may be called the aceto-propionic, being made up of an atom of each of these acids coupled together :

$$C_4 H_4 O_4 + C_6 H_6 O_4 = C_{10} H_{10} O_8 ;$$
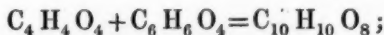
its bibasic nature is thus accounted for, and its formation meets with a curious parallel in the case of the pseudo-acetic acid of Nöllner.

This chemist† obtained by the fermentation of tartrate of lime, as prepared from crude tartar, a volatile acid which he termed pseudo-acetic acid. He described some of its salts, but did not analyse them. Nicklès,‡ however, undertook an investigation, from the results of which he concluded the acid to be a conjugate compound of butyric and acetic acids; he named it accordingly butyro-acetic acid. Berzelius considered it as a mixture of these two, while Dumas, Malaguti, and Leblanc, pronounced it to be identical with metacetonic (propionic) acid. However, from the decided character of some of the salts described, and the fact of the acid separating into butyric and acetic acids, neither of these views appears to be well founded.

The existence of the acid derived from citric acid lends a support to the original position of Nicklès, and furnishes another instance of the tendency of the acids $C_n H_n O_4$ to form coupled compounds. Viewed in this light, it is the lowest term yet known of a series of homologous conjugate acids, of which many members are wanting to render it complete. The properties of Lerch's§ vaccinic acid appear, upon consideration of the evidence, to class it among these bodies, although the amount of baryta found in the salt examined, differs

* Gmelin Handbuch, Band V, 112, 113.
† Ann. Ch. Pharm. XXXVIII, 299. Gmelin Handbuch, V, 115.
‡ Gmelin, V, 116.
§ Ann. Ch. Pharm. XLIX, 227.

somewhat from that corresponding to an acid composed of butyric and caproic acids. The circumstance of these acids being produced upon simple exposure to the air, and the identity of the saturating capacity of vaccinic acid with that of both the others, seem to overrule what may be an accident, and prove the acid to be a coupled body of the nature in question. This admitted, the terms of the series as yet known are :

Aceto-propionic acid . $C_{10} H_{10} O_8 = C_4 H_4 O_4 + C_6 H_6 O_4$
Butyro-acetic . . . $C_{12} H_{12} O_8 = C_4 H_4 O_4 + C_8 H_8 O_4$
Vaccinic . . . . $C_{20} H_{20} O_8 = C_8 H_8 O_4 + C_{12} H_{12} O_4$
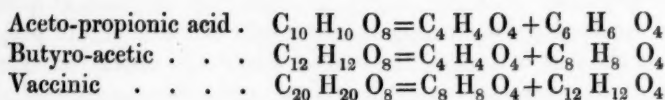
It was mentioned that the acid distillate from the soda-salt was received in three portions. Silver-salts were made from the two last in the same manner as from the first; they were decidedly more crystalline in appearance. A determination of the silver was made.

from II. $\begin{cases} 4\cdot702 \text{ grains, dried in vacuo, gave} \\ 3\cdot010 \quad ,, \quad \text{silver.} \end{cases}$

from III. $\begin{cases} 5\cdot270 \quad ,, \quad \text{dried in vacuo, gave} \\ 3\cdot385 \quad ,, \quad \text{silver.} \end{cases}$

Carbon			14·36	C_4	24
Hydrogen			1·19	H_3	3
Oxygen			19·76	O_4	32
Silver	64·01	64·23	64·69	Ag	108·1
	100·00	100·00	100·00		167·1

which is sufficient to show them to have the composition of acetate of silver; the peculiar odour of the liberated acid, and other reactions, confirmed this result.

The fact is here illustrated, that in a mixture of acids of this series, the most volatile does not invariably pass over first; the instance of an acid mixture in certain proportions of acetate and valerianate of potash, when distilled, is another case in point.

The derivation of these acids may be explained by the following scheme : if we add to the equivalents of two atoms of anhydrous citric acid, as it exists in the neutral lime-salt, the elements of 10 atoms of water, we obtain those of one atom of propionic, 2 of acetic, 10 of carbonic acid, and 6 of hydrogen.

$2 C_{12} H_5 O_{11} + 10 HO$ $= C_{24} H_{20} O_{32}$
$C_6 H_6 O_4 + 2 C_4 H_4 O_4$ $= C_{14} H_{14} O_{12}$

$$C_{10} H_6 O_{20} = 6 H + 10 CO_2$$
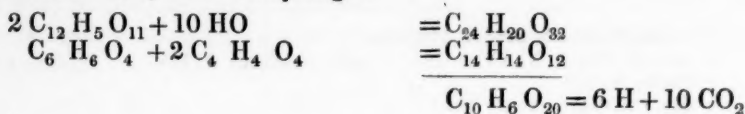
I made a second experiment upon a much larger scale, in the hope of obtaining a sufficient quantity of the aceto-propionic acid to enable me to study it more completely; but having somewhat varied the conditions, I obtained nothing but acetic acid. The details of the experiment are as follows :

Citric acid, as before, was neutralized with an excess of chalk, and curd to the amount of about a sixth part of the weight of the acid was added; the whole was mixed up to a thin paste with water, in an open glass vessel, which was then placed in a larger vessel of water, in which the temperature was kept constant at about 100° Fah., by means of a Kemp's apparatus. I observed, however, after fermentation had fairly commenced, that a thermometer immersed in the fermenting mass itself, always indicated a temperature about 10° higher than in the outer vessel. The process was continued between three and four weeks, at the end of which time, a quantity of filtered aqueous fluid was precipitated by sulphuric acid, and distilled. The product was received in three separate portions, as before ; a silver-salt was made from the first.

$$7 \cdot 315 \text{ grains, dried in vacuo, gave}$$
$$4 \cdot 710 \quad \text{,,} \quad \text{silver;}$$

the percentage calculated from this number is 64·38, while 64·69 is that of acetate of silver. Of a salt made from the last portion,

$$5 \cdot 916 \text{ grains, dried in vacuo, gave}$$
$$3 \cdot 825 \quad \text{,,} \quad \text{silver;}$$

calculated percentage = 66·65. I obtained a similar result by making a salt by direct precipitation of the lime-salt by nitrate of silver, the percentage of silver in the purified salt was found to be 64.

It is obvious, from the foregoing facts, that the nature of the product varies according to the conditions of experiment, and the comparatively high temperature constantly sustained was undoubtedly the cause of the formation of acetic acid only in the last case; it is possible that, by operating at a much lower degree of heat, either propionic, or aceto-propionic acid alone may be generated. Other results might be obtained with different salts of citric acid, with bases wanting the affinity for carbonic acid possessed by lime; some acid salts also might furnish subjects for experiments. I am not at present in a condition to supply any information on this subject; but should I arrive at any interesting facts in prosecuting some inquiries in this direction, which necessarily extend over a considerable length of time, I shall offer them to the notice of the Society.

II.—*On Populin.*

BY RAFAELLE PIRIA.

(FROM A LETTER TO DR. HOFMANN.)

Since my return to Italy, I have been engaged with the investigation of a crystalline substance, discovered, as you will recollect, by Braconnot in the leaves and bark of *Populus tremula*, and described by this chemist under the name of *Populin.* The composition and the reactions of this compound have remained unknown up to the present moment. From the following note, which gives you the results I have as yet obtained, you will see that populin is closely connected with several of the best known series of organic chemistry.

The composition of populin is represented by

$$C_{40} H_{22} O_{16} + 4 \, HO.$$
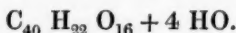
This formula, the result of direct analysis, is moreover confirmed by the deportment exhibited by this substance, when submitted to the influences of chemical agents.

On heating populin with dilute acids, it is decomposed into benzoic acid, grape-sugar, and saliretin, and you will observe that the above formula of crystallized populin exactly represents the sum of the elements of one equivalent of each of these substances.

$$\underbrace{C_{40} H_{26} O_{20}}_{\text{Crystallized populin.}} = \underbrace{C_{14} H_6 O_4}_{\text{Benzoic acid.}} + \underbrace{C_{12} H_{14} O_{14}}_{\text{Grape-sugar.}} + \underbrace{C_{14} H_6 O_2}_{\text{Saliretin.}}.$$
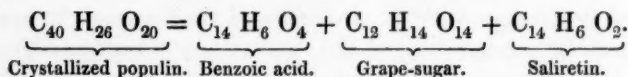
Since saliretin is a product of the action of acids on saligenin, populin may be viewed as a conjugate compound of benzoic acid with saligenin and grape-sugar.

$$\underbrace{C_{40} H_{26} O_{20}}_{\text{Crystallized populin.}} = \underbrace{C_{14} H_6 O_4}_{\text{Benzoic acid.}} + \underbrace{C_{12} H_{14} O_{14}}_{\text{Grape-sugar.}} + \underbrace{C_{14} H_8 O_4}_{\text{Saligenin.}} - 2 \, HO,$$
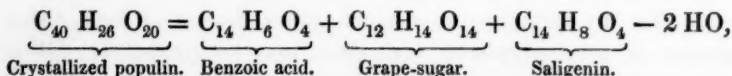
or, what amounts to exactly the same thing, as a conjugate compound of benzoic acid with salicin itself:

$$\underbrace{C_{40} H_{26} O_{20}}_{\text{Crystallized populin.}} = \underbrace{C_{14} H_6 O_4}_{\text{Benzoic acid.}} + \underbrace{C_{26} H_{18} O_{14}}_{\text{Salicin.}} + 2 \, HO.$$
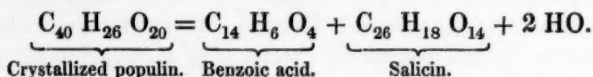
The relations which I have pointed out induced me to try whether

populin might not be converted into salicin. Nothing in fact is easier: it suffices to boil a solution of populin with baryta-water; you obtain a perfectly limpid liquid which contains nothing except benzoate of baryta and salicin. I have compared the chemical and physical properties of salicin thus obtained with those of the substances prepared from willow bark; they coincide in every point. Here then we have a very complex organic compound artificially produced by the decomposition of a still more complex substance.

My next step will be to transform, if possible, salicin into populin; I hope to effect this change by submitting it to the action of chloride of benzoyl.

$$\underbrace{C_{26}\ H_{18}\ O_{14}}_{\text{Salicin.}} + \underbrace{C_{14}\ H_{5}\ O_{2}\ Cl}_{\text{Chloride of benzoyl.}} = \underbrace{C_{40}\ H_{22}\ O_{16}}_{\text{Populin (anhydrous).}} + HCl.$$
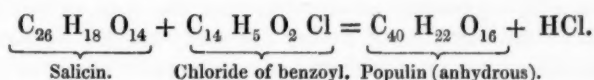
The only difficulty which presents itself as yet, is the action of the hydrochloric acid, which is liberated in this process, on the newly-formed compound.

I need scarcely mention, that in boiling populin with a mixture of sulphuric acid and bichromate of potassa, you obtain a considerable quantity of hydride of salicyl.

III.—*On the variation in the relative proportion of Potash and Soda present in certain samples of Barley grown in plots of ground artificially impregnated with one or other of these Alkalies.*

By CHARLES DAUBENY, M.D., F.R.S.,

PRESIDENT OF THE CHEMICAL SOCIETY OF LONDON.

Although the necessity for a due supply of earthy and alkaline matters to the growing vegetable may be at present regarded as indisputable, a good deal still remains to be done before we can pretend to lay down, with any degree of certainty, the extent to which any one of those ingredients, commonly present in a particular plant, may be replaced by others, without affecting its health or development.

Saussure,* indeed, had long ago ascertained, that a tree varied

* Recherches sur la végétation, 1804.

in its mineral constitution according to the nature of the soil in which it had grown; a fir, for instance, taken from a felspathic rock, being found by him to contain much potash, but no magnesia; whilst the same from a dolomitic rock was charged with magnesia, but exhibited a proportionate deficiency in alkali. Berthier,* also, had afterwards confirmed this inference by his analysis of two samples of oak timber, the one obtained from Norway, the other from Allevard, in Dauphiny, as the proportion of soda and of potash was found by him greater in the former instance than in the latter.

The independent results of these trustworthy chemists, Liebig† has endeavoured to bring under the operation of a general law, which he has himself suggested, in showing that the sum of the oxygen present in all the samples of timber analyzed, whether by Saussure or by Berthier, was uniformly the same, however much in relative amount the bases themselves might vary. This remarkable observation would certainly seem to favour the idea that, provided there be bases present in the soil sufficient for neutralizing the organic or mineral acids generated or secreted by the growing vegetable, the nature of the former was comparatively unimportant; and thus might lead us to conjecture, that isomorphous bodies, at least, which replace each other in the structure of a mineral, might do the same also in the organization of a plant.

Amongst other facts tending to the same conclusion, may be cited the analyses made some years ago by Will and Fresenius, of barley grown in the interior of Germany, and in the more maritime districts of the Netherlands, as the former was found to contain a smaller proportion of soda in comparison with the potash present, than the latter.

But before we allow ourselves to push our inferences beyond the point to which the above facts strictly warrant us in proceeding, let us consider, for a moment, the arguments that may be adduced on the opposite side, as tending to show, that a certain definite mineral composition is to be ascribed to each particular plant, and probably even to every one of the several organs of which it is made up. If the nature of the mineral ingredients present in a plant were a matter of indifference, provided only the neutralizing power possessed by them were sufficient for the purpose of enabling them to combine with the acids present; or even if, without proceeding to this extent, we suppose one alkali capable in general of supplying

* Ann. Ch. Phys. [2], LXXXII.
† Chemistry in its application to agriculture, &c.

the place of another, or an alkaline earth of being substituted for an alkali, what then is the end of that remarkable power of selection which all plants possess, and which is so remarkably evinced by those of marine origin, in their assimilation, not only of iodine, but also of potash, from a sea containing both in infinitesimal proportions only. The case of the Algæ, indeed, is only an extreme example of a generally pervading law; for it is sufficient to cast a glance over any series of vegetable analyses, as, for instance, the tabular view given by Dr. Karl Bischof in a late number of the "Journal für praktische Chemie,"* of the composition of various plants, to be convinced, that they in general absorb potash in preference to, and even to the exclusion of, soda, without reference to the comparative abundance of the two alkalies in the soil.

Dr. Bischof shows, that out of a series of 200 ash analyses of land plants, or of particular portions of them, there are more than $\frac{4}{7}$ths in which the proportion of potash was estimated to exceed that of soda, and more than $\frac{1}{5}$th in which potash alone was found, these latter analyses moreover being the most recent, and probably, therefore, the most trustworthy. On the other hand, there is not a single plant known in which soda alone occurs, and only a few, excepting those belonging to the class of marine algæ, in which its amount exceeds that of potash. Bischof also assigns reasons for supposing that the proportion of soda in the ashes may often have been over-estimated. It seems, moreover, difficult to understand, why, if soda can take the place of potash, and lime or magnesia of either, the same should not be the case with strontia; and yet I found several years ago,† that when a plant had been watered with a solution containing that earth, so minute a trace of it was found in its ashes, that it became impossible to suppose the principle in question to have entered into the composition of its tissue. Lastly, with reference to the results obtained by Will and Fresenius, I may be permitted perhaps to set against them, some made a few years ago in my own laboratory, which tended to show, that barley possessed the same mineral composition, so far as its alkalies were concerned, whether it had been grown in the east or west coasts of England, or in the more central district of Oxfordshire.‡

Deeming, therefore, the subject to be one open to further investigation, I was induced last summer to institute a few experiments;

* Vol. XLVII.
† Linnean Trans. 1833.
‡ Bakerian Lecture on the rotation of crops, in the Ph. Trans. for 1845.

the results of which I will next submit, as introductory to a statement of certain views respecting the mode in which the two alkalies come to be formed in the ashes of a plant, and the functions severally discharged by them in their living organisation, which I am desirous of laying before this Society.

For the purpose of ascertaining how far the alkaline constitution of a crop of barley might be modified by a difference in the quality of the soil in which it was grown, I selected in the same part of the Oxford Botanic Garden, seven plots of ground, of equal size, and as nearly as possible similar in point of quality, exposure, &c. Two of these plots were manured with a pretty strong dressing of sub-carbonate of potash; two with an equivalent amount of subcarbonate of soda; two with common salt, in quantity sufficient to supply the same proportion of soda as the last; whilst the seventh was left without any application at all. The size of the plots was such, that the quantity of potash added would be equivalent to about ten bushels of common salt to the acre, and to corresponding quantities of carbonate of soda, and of carbonate of potash to the same surface of soil.*

In order to prevent these saline matters from being too speedily washed away by rain, I had previously dissolved them in water, and had mixed each of the several solutions with a bulk of stiff clay large enough to absorb the whole of the liquid. The mixture was then exposed to the sun and air, in order that the salts might become dry, and be thoroughly incorporated with the mass; after which the whole was thrown upon the plots intended for their reception, and mixed up intimately with the soil down to the depth of two feet from its surface.

An equal amount of barley was then sown in each of the said plots, and the crop obtained separately dried and weighed, the straw and grain having been kept distinct. A portion of each having been then incinerated, the soluble portion of the ash was taken up by water, after which everything, except the alkaline salts, was removed by the methods usually employed for that purpose. An aliquot portion of the alkaline residuum was in each case converted into chloride, and the potash separated from the soda-salt by means of the chloride of platinum.

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* The quantities being respectively :

> 7 lbs. of pearl-ash,
> 20 „ of subcarbonate of soda in crystals,
> 9 „ of common salt to each plot,

these numbers representing equivalent amounts of the two alkalies.

The following were the results obtained by this method :

Manured with:	PLOTS :			
	yielded :			in 100 parts of the alkaline residuum.
	altogether.		of :	
				Potash. / Soda.
Carbonate of potash . {	average of the two crops } 71¼ lbs.		viz. { grain 13½ lbs. / straw 58 „	84·50 / 15·50 79·50 / 20·50
Carbonate of soda . {	„ „ 71 „		viz. { grain 13½ „ / straw 57½ „	76·50 / 23·50 72·75 / 27·25
Chloride of sodium . {	„ „ 78 „		viz. { grain 14½ „ / straw 63¾ „	76·50 / 23·50 76·50 / 23·50
Unmanured.	produce of the bed . . . } 63 „		viz. { grain 11 „ / straw 52 „	82·50 / 17·50 79·50 / 20·50

The difference between the amount of produce, in the bed left unmanured, and in the rest, sufficiently attests the benefit that had been derived from every one of the saline matters added, and that nearly in an equal ratio from each of them; whilst the larger amount of soda present in the crops which had been dressed with carbonate of soda and with chloride of sodium, might seem to indicate, that this alkaline principle had, to a certain extent, taken the place of the potash, in consequence of its being present in the soil in a larger proportion here than in the other plots.

But a little further consideration may perhaps suggest a different mode of explaining the facts in question. It must be recollected in the first place, that the roots of plants suck up indiscriminately from the soil every kind of matter presented to them, whether it be poisonous to them or nutritious, as was long ago ascertained to be the case by Saussure.

There must, therefore, be circulating through the system of a plant, during all the stages of its growth, a certain amount of every species of saline matter which happens to lie in contact with its roots, of which, although only that which is capable of being assimilated by its organs actually constitutes a part of its substance, the remainder is nevertheless detained within the vegetable tissue for a certain time, and cannot be separated from it by any known mechanical process.

When therefore we dry a plant, and reduce it to ashes, its residuum after incineration will contain, not only the alkaline matter which actually entered into the composition of the organs themselves, but likewise that circulating at the time through its tissue. The former

the results of which I will next submit, as introductory to a statement of certain views respecting the mode in which the two alkalies come to be formed in the ashes of a plant, and the functions severally discharged by them in their living organisation, which I am desirous of laying before this Society.

For the purpose of ascertaining how far the alkaline constitution of a crop of barley might be modified by a difference in the quality of the soil in which it was grown, I selected in the same part of the Oxford Botanic Garden, seven plots of ground, of equal size, and as nearly as possible similar in point of quality, exposure, &c. Two of these plots were manured with a pretty strong dressing of sub-carbonate of potash; two with an equivalent amount of subcarbonate of soda; two with common salt, in quantity sufficient to supply the same proportion of soda as the last; whilst the seventh was left without any application at all. The size of the plots was such, that the quantity of potash added would be equivalent to about ten bushels of common salt to the acre, and to corresponding quantities of carbonate of soda, and of carbonate of potash to the same surface of soil.*

In order to prevent these saline matters from being too speedily washed away by rain, I had previously dissolved them in water, and had mixed each of the several solutions with a bulk of stiff clay large enough to absorb the whole of the liquid. The mixture was then exposed to the sun and air, in order that the salts might become dry, and be thoroughly incorporated with the mass; after which the whole was thrown upon the plots intended for their reception, and mixed up intimately with the soil down to the depth of two feet from its surface.

An equal amount of barley was then sown in each of the said plots, and the crop obtained separately dried and weighed, the straw and grain having been kept distinct. A portion of each having been then incinerated, the soluble portion of the ash was taken up by water, after which everything, except the alkaline salts, was removed by the methods usually employed for that purpose. An aliquot portion of the alkaline residuum was in each case converted into chloride, and the potash separated from the soda-salt by means of the chloride of platinum.

* The quantities being respectively :

> 7 lbs. of pearl-ash,
> 20 „   of subcarbonate of soda in crystals,
> 9 „   of common salt to each plot,

these numbers representing equivalent amounts of the two alkalies.

The following were the results obtained by this method :

Manured with:	altogether.		of:		in 100 parts of the alkaline residuum.	
PLOTS :			yielded :			
					Potash.	Soda.
Carbonate of potash . {	average of the two crops } 71½ lbs.		viz. {	grain 13¼ lbs.	84·50	15·50
				straw 58 „	79·50	20·50
Carbonate of soda . {	„ „ 71 „		viz. {	grain 13¼ „	76·50	23·50
				straw 57½ „	72·75	27·25
Chloride of sodium . {	„ „ 78 „		viz. {	grain 14½ „	76·50	23·50
				straw 63¾ „	76·50	23·50
Unmanured.	produce of the bed . . . } 63 „		viz. {	grain 11 „	82·50	17·50
				straw 52 „	79·50	20·50

The difference between the amount of produce, in the bed left unmanured, and in the rest, sufficiently attests the benefit that had been derived from every one of the saline matters added, and that nearly in an equal ratio from each of them; whilst the larger amount of soda present in the crops which had been dressed with carbonate of soda and with chloride of sodium, might seem to indicate, that this alkaline principle had, to a certain extent, taken the place of the potash, in consequence of its being present in the soil in a larger proportion here than in the other plots.

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When therefore we dry a plant, and reduce it to ashes, its residuum after incineration will contain, not only the alkaline matter which actually entered into the composition of the organs themselves, but likewise that circulating at the time through its tissue.   The former

indeed, may be assumed to bear a constant relation to the volatilizable ingredients associated with it, but the latter will necessarily vary according to the nature of the saline impregnation belonging to the water which bathes its roots.

Thus, from the soil to which nothing had been added, a certain amount of soda as well as of potash would seem to have been extracted by the barley grown in it, since both alkalies made their appearance in the portions incinerated. This, however, is easily explained, inasmuch as, by a previous analysis, both soda and potash had been found to exist as original constituents of the soil. It is probable, however, that a good deal of the estimated quantity of each did not actually enter into the constitution of the organs, but had been merely arrested in its progress through the plant, so as to be present in it at the moment when the crop was cut down.

From the addition of carbonate of potash to the soil, only a small increase to the percentage of potash in the plant itself appears to have resulted; but it must be recollected, that the quantity of potash present in the ground was distributed over a greater amount of crop, as the produce of the beds rose, in consequence of this addition, from 63 to 71$\frac{1}{2}$ lbs.

By the dressing of carbonate of soda given to the third set of beds, the percentage of soda was augmented in a still higher ratio, because the increase of crop which followed did not in the same degree augment the consumption of soda by the plant, as this alkali enters less abundantly into its actual organisation. A larger proportion of it, therefore, would remain in the juices circulating through the vegetable tissue, and would therefore add to the apparent amount of soda in the crop when examined.

The same explanation may apply to the increase of the same alkali which took place in the crop that had been manured with common salt; this, however, would appear to exist in the plant as common salt, since, judging from the results of the analyses given in my Bakerian Lecture,* the salt in question enters, as such, into the tissue of a plant without undergoing decomposition.

I may perhaps elucidate my meaning by the following hypothetical statement, in which the numbers given must be understood to be quite arbitrary, and intended merely for the purpose of illustration.

Confining ourselves to the grain of the barley experimented upon, let us assume the normal quantity of potash and soda present in it to stand to each other in the relation of 74 of the former to 9 of the latter.

* Phil. Trans. for 1845.

Then, in the unmanured crop :

Normal quantity being . .   Potash 74·0   Soda   9·0
There will have been circu-
   lating through the crop
   when cut . . . . .   „   8·5   „   8·5 or 50 to 50.
                                       82·5   17·5

In crops manured with carbonate of potash :

Normal quantity . . . .   Potash 74·0   Soda   9·0
Circulating through the crop   „   10·5   „   6·5 or 67 to 33.
                                       84·5   15·5

In the crops manured with carbonate of soda and chloride of sodium :

Normal quantity . . . .   Potash 74·0   Soda   9·0
Circulating through the crop   „   2·5   „   14·5 or 15 to 85.
                                       76·5   23·5

The above explanation may perhaps be open to objection ; but I conceive it to be at least encumbered with fewer difficulties than would attend the notion of an actual substitution of soda for potash taking place within the organism of a plant ; for in that case we must suppose, that although a certain number of the atoms of the one alkali may be replaced by the other, no such change can take place with regard to the greater part of those present ; for were the latter possible, that is, were the whole, or the greater part of the atoms of potash capable of being replaced by soda, not only would there have been a much greater difference in the constitution of barley grown in soils so largely impregnated, as mine were, with salts of soda, in comparison with the same charged with those of potash ; but we should also be at a loss to explain the absence of a larger proportion of soda-salts in those samples of barley which I had obtained from the neighbourhood of the sea, than existed in others taken from inland situations.

In the experiments above detailed, the utmost increase of soda in the crop, caused by so liberal an application of soda-salts to the soil, did not exceed 8 per cent of the whole ; or in other words, if we adopt the hypothesis of substitution, only 1 atom in 12 of the potash actually present admitted of being replaced by soda : nor does it

appear, that the largest disproportion between the quantity of the two alkalies brought into contact with the plant can materially affect this limitation; for otherwise, marine algæ, which are nourished by a fluid in which the potash stands in the smallest possible relation to the soda, could scarcely contain so large an amount of potash as is frequently found to exist in them. And yet, although we must, in adopting this hypothesis, assume certain limits to exist, beyond which the usual constitution of a plant does not admit of change even by the most liberal supply of soda, a large excess of this latter alkali must be supposed necessary, in order that it should replace the potash in any degree at all; inasmuch as we find no extraordinary amount of the mineral alkali in barley grown near the sea, where soda-salts must be more abundant than they are inland.

These considerations would lead me to imagine, that even in marine plants, a portion of that large quantity of soda, which is detected in their ashes, may be derived from the juices circulating through their cellular structure, and does not enter into their actual organisation; so that even in them, perhaps, potash may turn out to be the alkali which plays the principal part in building up the living fabric of the plant. I am by no means inclined, however, to limit the uses of the alkaline matter which is constantly contained in the sap, to the one end of supplying a plant with the potash and soda, which it requires, for the formation of its different organs, and for that of its characteristic secretions; since Liebig himself has pointed out another function which both alkalies are equally fitted to discharge, namely, the fixation of carbonic acid, through which, owing to the consequent diminution of oxygen, sundry other organic acids, such as the tartaric, the oxalic, the malic, &c. may be formed.

It is not my intention, however, to pursue this fertile subject on the present occasion; in conclusion, therefore, I will only remark, that I am fully aware of the scantiness of the data contributed by myself in this paper towards the elucidation of the question discussed in it; and that I should have been reluctant to occupy the time of this Society by bringing them forward, had I not hoped that they might be the means of stimulating others of our members, who have more leisure than myself, for such investigations, to undertake a larger and more precise train of experiments, calculated to determine the still questionable point, as to the power residing in plants to substitute one mineral ingredient for another, in the construction of their respective organs, or in the elaboration of the peculiar secretions which they contain.

IV.—*On the Compounds of Cotton with the Alkalies.*

By J. H. GLADSTONE, PH. D.

THE beautiful effects produced by Mr. Mercer through treating cotton with a cold solution of caustic soda, are well known not only to the scientific world, but, through the medium of the Great Exhibition, to the public in general. Yet I believe the chemical compound tself has not hitherto been investigated.

This gentleman found that when cotton, or a cotton fabric is immersed in a very strong alkaline ley in the cold, a certain combination is effected. This "sodaed" cotton parts with all its alkali when washed with pure water, and the "mercerized" cotton thus produced, is not only much contracted, so that coarse fabrics have assumed the appearance of fine ones, but when dyed it displays colours of more than ordinary brilliancy.

It is evident that, by the process described above, the combination of soda and lignine is not obtained in a state fit for analysis. As the fabric issues from the alkaline ley, there adheres to it an excess of soda, and the moment it is touched by water its integrity is destroyed. It became a desideratum then to find a solvent capable of removing the uncombined alkali whilst it left the compound unimpaired. Alcohol suggested itself to my mind as likely to possess the requisite quality, especially as it might be employed in an anhydrous condition.

As preliminary experiments, two portions of pure cotton were taken, each weighing 20 grs. when thoroughly dried. The one was steeped in cold caustic soda, so dilute as not to produce Mr. Mercer's reaction, the other in a strong solution of soda. They were both soaked repeatedly in successive portions of absolute alcohol, and subsequently dried in vacuo over sulphuric acid. In Exp. I. the cotton proved to be of the original weight, and did not retain any soda; in Exp. II. the cotton had increased to 24·4 grs., and contained an amount of soda, which, when dissolved out by water, neutralized by sulphuric acid, and evaporated in a platinum dish (excess of sulphuric acid in combination being removed as usual by small pieces of carbonate of ammonia), gave 4·8 grs. of sulphate= 2·1 grs. of absolute soda. From the first experiment, the conclusion may be drawn that absolute alcohol is capable of removing from cotton any portions of uncombined soda; and from the second it may be inferred that such alcohol does not decompose the compound of soda and cotton.

Having thus obtained a method, I performed a series of more exact experiments. A solution of soda of sp. gr. 1124 was found capable of combining with cotton, though it did not produce much shrinking. It was made use of in preference to a stronger solution, as it left less alkali adhering to the fibre to be afterwards washed out with alcohol.

Exp. III. 20 grs. of cotton steeped for an hour in the alkaline ley, washed repeatedly with absolute alcohol, and thoroughly dried in vacuo, had increased to 21·97 grs., and furnished 2·70 grs. of sulphate of soda.

Exp. IV. The cotton regained from Exp. II., similarly treated, showed an increase in weight to 21·09 grs., and yielded 2·71 grs. of sulphate of soda.

Exp. V. 20 grs. of cotton were treated in precisely the same manner, but as the difficulty of washing out the uncombined soda consumed much absolute alcohol, ordinary rectified spirits was employed instead. The soda compound weighed 21·28 grs., and yielded 2·05 grs. of sulphate of soda.

Exp. VI. 20 grs. of cotton similarly treated, were washed with hot alcohol of sp. gr. 825. The dried compound weighed 22·20 grs., and yielded 3·12 grs. of sulphate. This is a large amount, and indicates that alcohol of this strength may safely be employed to wash the compound.

Exp. VII. Lest it might be contended that the alcohol did not remove from the woody fibre certain impurities, which might be present in an aqueous solution of soda, 20 grs. of cotton were steeped in a clear but saturated alcoholic solution of the alkali. Little if any shrinking took place, but there was a certain amount of combination, for the cotton well washed with spirits of sp. gr. 825 and dried, weighed 21·01 grs., and afforded 1·41 grs. of sulphate of soda.

As yet the results are very discordant, as will be apparent from the annexed table, nor does the combined soda in any instance stand in a definite atomic ratio to the lignin:

	Ratio between original and soda-ed cotton			and combined soda.	
Exp. III.	100	:	109·85	:	5·91
,, IV.	100	:	105·45*	:	5·94
,, V.	100	:	106·4	:	4·49
,, VI.	100	:	111·0	:	6·83
,, VII.	100	:	105·05	:	3·08

* This number is reckoned as obtained from 20 grs.; but it is in all probability too low, since the whole amount of cotton, as will be afterwards explained, is never recovered from the mercerizing process.

From this we must conclude either that woody fibre has a great affinity for caustic soda at a low temperature, but does not form any definite chemical compound with it ; or else that the cotton in the forementioned experiments had not been thoroughly saturated with the alkali.   As this might depend upon the strength of the alkaline ley in which the immersion was made, a solution of soda of sp. gr. 1342 was employed, and gave much more satisfactory results.

Exp. VIII. 20 grs. of cotton steeped in soda-solution of the above-mentioned specific gravity, and washed with successive portions of hot alcohol of sp. gr. 825, until when dried it ceased to lose weight, was found to have increased to 22·64 grs., and yielded 4·25 grs. of sulphate of soda.

Exp. IX. 20 grs. of previously mercerized cotton, similarly treated, showed an increase of weight to 23·21 grs., and yielded 4·70 grs. of sulphate.

Exp. X. A piece of calico 4 in. × 4, and weighing, when thoroughly dried, 18·65 grs., was subjected to the action of soda.   From a solution of sp. gr. 1124 it absorbed an amount of soda equivalent to 2·00 grs. of sulphate; that is, as 100 : 4·70 combined soda.   Washed with water, dried, again immersed in alkaline ley, but of sp. gr. 1342, washed with hot alcohol of sp. gr. 825, and dried in vacuo, it weighed 21·84 grs., and yielded 4·40 grs. of sulphate of soda.   The immersion in soda only lasted 10 minutes.   The piece of calico had contracted to the measure of 3·3 in. × 3·3.

Exp. XI. In order to ascertain whether the fibre was capable of combining with a still larger proportion of soda, either by employing a stronger alkaline ley, or by exposing it to the action for a longer period, a piece of calico weighing 18·32 grs. was immersed for 17 hours in a solution of caustic soda so strong as to be syrupy, in a vessel protected from the atmosphere.   Having been washed and dried as usual, it weighed 21·04 grs., and yielded 3·78 grs. of sulphate of soda.   This, instead of being a larger amount of soda than in the three previous instances, is a trifle smaller.   There was the same amount of contraction.

Exp. XII. was intended as one in which every precaution should be taken to insure the definite character of the compound examined. A piece of fine calico of about 90 strands to the inch, weighing 14·67 grs., and measuring 3 in. × 3, was steeped in cold caustic soda in a close vessel for 30 minutes.   It was then removed, pressed between folds of cloth, and washed with absolute alcohol also in a vessel protected from the air, until it ceased to lose weight when dried.   Dried

in vacuo it weighed 17·17 grs., and it afforded 3·15 grs. of sulphate of soda.

The results of these five experiments may be thus tabulated:

	Ratio between original and soda-ed cotton			and combined soda.	
Exp. VIII.	100	:	113 2	:	9·31
„ IX.	100	:	116·05	:	10·30
„ X.	100	:	111·2	:	10·34
„ XI.	100	:	114·8	:	9·07
„ XII.	100	:	117·05	:	9·41

It will be at once evident that there is a wide discrepancy between the numbers in the first column, but the second column presents considerable accordance; and, if we take the amount of soda in the experiment most to be relied on—No. XII., namely, 9·41 per cent, or the average of the whole five determinations,—namely, 9·68 per cent, we find it almost exactly coinciding with the amount that should be obtained, supposing one atom of soda to combine with one atom of lignine—$C_{24} H_{20} O_{20}$—namely, 9·65.

$$324 \ : \ 31·3 \ :: \ 100 \ : \ 9·65.$$

The mode of production of this substance might lead us to imagine that it was a substitution product of $C_{24} H_{20} O_{20}$, in which one equivalent of sodium replaced one equivalent of hydrogen; but, as the weight of the dried substance never fell short of the united weights of the cotton and the soda taken up, it must rather be considered as a compound of the two. The difference of its state of hydration clearly gives rise to the differences observable in the first column of the tables. In some instances (as Exp. X.) the soda appears to carry along with it little or no water, in other instances (as Exp. XII.) as large a quantity as 3 equivalents; and this combined water will not separate in vacuo at ordinary temperatures. The compound is also very hygroscopic, absorbing from moist air, in one observed instance, as much as 5·39 grs. of water for 23·21 grs. of "soda-ed" cotton, which however it parted with again in vacuo. When neutralizing with sulphuric acid the soda washed out from the cotton, I had frequently observed that there was no effervescence: this induced me to try whether the "soda-ed" cotton really did not absorb carbonic acid. Upon exposing a portion to an atmosphere of this gas, I found the alkali was converted into carbonate; and 20 grs. of cotton, which proved to be combined with 2·06 grs. of soda, weighed when dried in vacuo 23·71 grs. Little or no water could have been retained by the

substance, for the weight of the cotton, plus that of the alkali consi-dered as carbonate, would be 23·51 grs. There is a remarkable circumstance attending this compound in its relation to heat: it becomes scorched at a far lower temperature than the original cotton.

That the combination of the soda with the cotton has effected a permanent change upon it is certain; when regained it is contracted, and takes dyes better; but the question arises: Is this merely a physical alteration, or has a real chemical change of the lignina taken place? I am inclined to view the "mercerized" cotton as chemically identical with the original substance. In the first place, it is of the same ultimate composition. It is true, the cotton regained never absolutely equalled the original in weight; but it was always observed that the fibre lost some flocculent portions during the steeping and the washing processes, enough to account for the 1 or 1·5 per cent deficiency which usually occurred. The removal of only one equi-valent of water would have occasioned a decrease of 2·78 per cent. Again, the mercerized cotton can be recombined with soda, causing even some additional shrinking by the process. Mixed nitric and sulphuric acids convert it into gun-cotton; it is acted upon by oil of vitriol just as ordinary lignine; and it is similarly hygroscopic.

The change that takes place in the physical condition of the cotton is best observed under the microscope. The fibres in their ordinary state appear as flattened twisted ribands; but the moment they are touched by the alkaline ley they untwist themselves, and contract in length, as they swell out, assuming a rounded solid form; and this circular appearance they retain after the soda is removed by water. Thus the shrinking is explained, and I think also the superior character of the colours which mercerized cotton is capable of exhi-biting. For the substance of the fibre itself is of a porous nature, and will of course absorb a larger quantity of the dye when expanded, than when compressed into a flat twisted band, and as this takes place in the same space, a greater *intensity* of colour must be the result.

From these observations it appears that lignine is capable of forming a combination with soda, the proportion of the alkial varying with the strength of the solution employed, but in no instance exceeding one atom, and that this compound is decomposed by water, being resolved into its original compounds.

In order to ascertain whether a similar potash compound existed, a piece of fine calico, measuring 3 in. × 3, and weighing 14·50 grs., was immersed for thirty minutes in as strong a solution of potash as

could be obtained limpid. It was washed with alcohol of sp. gr. 825, and dried and decomposed as usual. It shrank to the dimensions of 2·7 in. × 2·7. When combined with potash it weighed 17·14 grs., and it yielded 3·83 grs. of sulphate of potash.

<div align="center">
Ratio between
original and combined cotton   and potash.
</div>

Exp. XIII. . . .   100 : 118·2 | : 14·27

This shows that there was one equivalent of potash taken up by the cotton, the compound being $C_{24} H_{20} O_{20} + KO$.

$$324 : 47\cdot3 :: 100 : 14\cdot59.$$

These compounds of the alkalies with lignine are clearly analogous to their known compounds with sugar. Brendecke and others have shown that both cane- and grape-sugar will combine with potash and soda in the proportion of 1 equivalent, $C_{24} H_{20} O_{20}$, to 1 equivalent of the alkali. Whether these compounds are decomposed by water does not appear from the recorded observations; for whether it be so or not, the same phenomena would be presented. Disregarding the varying amount of water combined with the lignine compounds, we find both them and the sugar compounds expressed by the formulæ :

$$C_{24} H_{20} O_{20}.\ KO,\ \text{and}\ C_{24} H_{20} O_{20}.\ NaO.$$
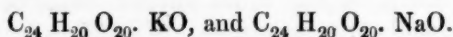
V.—On the occurrence of Capric and Caprylic acids in some Fousel oils

BY THOMAS H. ROWNEY, F.C.S.,

ASSISTANT IN DR. ANDERSON'S LABORATORY, EDINBURGH.

In a paper read before the Royal Society of Edinburgh and published in their Transactions,[*] I pointed out that capric acid could be obtained from the fousel oil procured from some of the Scotch distilleries. At the same time, I mentioned that another acid was present, but in such small quantity that its constitution could not be ascertained.

The capric acid was found in the residue obtained after distilling off the amylic alcohol, and in that portion of the residue having the

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* Vol. XX, Part 2nd. p. 219; abstr. Chem. Soc. Qu. J. IV. 372.

highest boiling point, viz., above 240° C.   A subsequent examination of the portion boiling between 190° C. and 220° C., enabled me to obtain a sufficient quantity of the second acid to determine its composition.

The oily residue was boiled with a strong solution of caustic potassa; dilute sulphuric acid was added to the cold alkaline solution; and the oil which rose to the surface was filtered off and washed with cold water; it was then dissolved in a solution of ammonia and precipitated by chloride of barium, and this precipitate was collected on a filter and washed with cold water.   The baryta-salt was dissolved in boiling water, filtered, and allowed to crystallize; the crystals obtained were caprate of baryta. This salt was separated by filtering, and the mother-liquor was concentrated by evaporation on a water-bath. When reduced to about one-third of its bulk, it was allowed to cool, when it deposited an abundant crop of crystals; the mother liquor from these crystals gave another crop by being again concentrated. The baryta-salt was purified by re-crystallization, and an analysis made of it.   The baryta was determined as carbonate, by ignition in a platinum crucible, the salt burning very readily:

I.

·2872 grms. of substance, dried at 100°C., gave
·1340   ,,   ,, carbonate of baryta.

II.

·3300 grms. of substance gave
·1535   ,,   ,, carbonate of baryta.

III.

·2930 grms. of substance gave
·1360   ,,   ,, carbonate of baryta.

IV.

·2705 grms. of substance, dried. at 100°C., and burnt with
                         chromate of lead, gave
·4487   ,,   ,, carbonic acid, and
·1772   ,,   ,, water.

V.

·2973 grms. of substance gave
·4940   ,,   ,, carbonic acid, and
·1988   ,,   ,, water.

	I.	II.	III.	Mean.
Ba O	36·24	36·12	36·04	36·13.

	IV.	V.	Mean.
Carbon	45·24	45·31	45·28
Hydrogen	7·28	7·42	7·35.

The numbers obtained, correspond with those for caprylate of baryta, as will be seen by comparing the theoretical numbers with those obtained by experiment.

			Mean of experiment.
C_{16}	96	45·37	45·28
H_{15}	15	7·09	7·35
O_3	24	11·34	11·24
BaO	76·6	36·20	36·13
	211·6	100·00	100·00

This examination shows, that, in addition to the usual constituents of fousel-oil, viz., water, alcohol and amylic alcohol, the fousel-oil obtained from some of the Scotch distilleries, contains compounds having a higher boiling point than amylic alcohol, and that capric and caprylic acids are present in these compounds, but whether as amyl or ethyl compounds could not be ascertained, as no fixed boiling point could be obtained on distillation.

VI.—On the oxidation of Chinese wax.

By Nevil S. Maskelyne, M.A.,

DEPUTY READER IN MINERALOGY TO THE UNIVERSITY OF OXFORD.

The experiment which I propose to describe, suggested itself in the course of an investigation commenced by me in the laboratory of Mr. Brodie in the early part of last year, but which has been interrupted by unavoidable circumstances, and only recently resumed. Without entering upon the other questions involved in that investigation, it is only necessary to state that it embraced the inquiry into the chemical nature of the substances which we know as Chinese wax and spermaceti.   When isolated from certain slight impurities which it contains, Chinese wax has the formula $C_{108} H_{108} O_4$, which, by the action of hydrate of potash, may be broken up into substances with

the formulæ $C_{54} H_{56} O_2$ [cerotin] + $C_{54} H_{54} O_4$ [cerotic acid], two equivalents of water being assumed in the saponification. If instead of melting the Chinese wax with hydrate of potash with a view to saponify it, it be mixed with lime and potash, and heated gently in a large combustion tube, a change takes place in the substance, which is of a definite character, and therefore easily controlled. Hydrogen gas is evolved at the part of the tube where the heat is applied; and so soon as this evolution ceases, the coals should be removed to another part of it. The product resulting from this oxidation of the wax is, as will be seen, a salt of cerotic acid, and if the process be carefully performed, this forms a very neat, indeed the best way of procuring this wax-acid.

$5\frac{1}{2}$ oz. of potash-lime were taken to oxidize 1 oz. of Chinese wax. The resulting mass was boiled for a long time with hydrochloric acid; the wax matter thus eliminated was then frequently boiled with water, and finally dissolved in alcohol, and filtered while hot. A little undissolved substance remains on the filter, but it is only in very minute quantity. On the cooling of the alcohol, the dissolved substance forms a copious white precipitate of which the melting point is 79°—80° C. The acid, however, is not pure; for here, as is probably also the case with spermaceti, there is present a contaminating substance in small quantity, which it is very difficult to separate completely. The mass of acid has to be dissolved and crystallized two or three times out of alcohol, and finally once or twice out of ether. The ether holds in solution the substance alluded to, which exists in very small quantity, and has a melting point at least as low as 69°. The acid, as thus obtained, is pure cerotic acid. Its melting point is 81°, 82°, and it yielded, on being analyzed, the following numbers:

I. ·2332 grms. gave   ·6771 CO_2 and ·2725 HO
II. ·2110 „   „   ·6118   „   ·2536
III. another preparation,
      ·2355 „   „   ·6814   „   ·2841

which correspond to the following per-centage of carbon and hydrogen:

	I.	II.	III.	Theory requires.
Carbon	79·19	79·07	78·90	79·02
Hydrogen	12·98	13·35	13·41	13·17
Oxygen	7·83	7·58	7·69	7·81
	100·00	100·00	100·00	100·00

The silver-salt was formed by means of an alcoholic solution of nitrate of silver, and a solution, also in alcohol, of an ammonia-salt of the acid in the presence of an excess of ammonia. It yielded the following per centage of silver :

$$6 \cdot 10 \text{ grs. gave } 1 \cdot 280 \text{ grs.} = 20 \cdot 98 \text{ per cent}$$

$$4 \cdot 81 \text{ ,, ,, } 1 \cdot 010 \text{ ,, } = 20 \cdot 99 \text{ ,,}$$

Theory requires $20 \cdot 90$,,

There can, therefore, be little question as to the character of the change thus wrought by the oxidizing action of the potash-lime. Regarding the wax as the homologue of acetic ether, the acid has its origin in two sources.   On the one hand, the ether, of which cerotin is the corresponding alcohol, is oxidized into cerotic acid, while on the other hand, the anhydrous cerotic acid, which on this view is supposed to be combined with that ether, unites with the alkali, the process being divided into two parts, first, the saponification of the substance, and subsequently the oxidation of the alcohol formed from the ether by that saponification.   On another view, first propounded by Mr. Lawrence Smith in relation to spermaceti, we may look upon these bodies as homologues of aldehyde, in which case the wax may be regarded as the aldehyde of cerotic acid, its formula being halved $[C_{108} H_{108} O_4 = 2 (C_{54} H_{54} O_2)]$.   Regarding it in this light, the oxidation is that of the substance as a whole into cerotic acid, $C_{54} H_{54} O_2 + O_2 = C_{54} H_{54} O_4$. The present experiment does not decide between these two views. I have made some further experiments in this direction, which I hope on a future opportunity to communicate to the Society. The process I have described is important, as furnishing by far the most expeditious method we at present possess of procuring cerotic acid; for the washing out of the baryta-salt, formed in the treatment of the Chinese wax, or of the lead-salt of cerotic acid from common bees-wax, is a most tedious operation.

Spermaceti is a body precisely identical in type with Chinese wax. I have oxidized this substance also, in the expectation that the result would clear up the doubt as to the identity or otherwise of ethalic and palmitic acids.   These experiments do not belong to the history of Chinese wax, and it will therefore be preferable to make them also the subject of a future communication.

On a quick approximative method of estimating minute quantities of iron by means of a Colorimeter. By THORNTON J. HERAPATH.

The author having been much occupied with the analysis of waters containing minute quantities of iron, and finding the ordinary mode of estimation by precipitation and weighing very troublesome and inaccurate, when applied to such quantities, was led to avail himself of the following centigrade method, founded on the reaction of persalts of iron with sulphocyanide of potassium. A standard solution of perchloride of iron containing a little less than $\frac{1}{100}$th of a grain of metallic iron per cent, was prepared by dissolving 1 grain of iron in hydrochloric acid, with the addition of a little nitric acid, evaporating nearly to dryness, and diluting to 10,000 gr. measures with distilled water at $60°$; and from this, other standard solutions of different strengths were formed. A convenient quantity of the water, generally half a gallon, was evaporated to dryness, and the saline mass so obtained was afterwards dissolved in hydrochloric acid. The iron contained in the solution having been converted into perchloride by boiling with a few drops of nitric acid, the silica and other insoluble substances were separated by filtration, and the peroxide of iron precipitated by ammonia. This latter precipitate was collected on a filter, and well washed with water. It was then redissolved in the smallest possible quantity of hydrochloric acid, and the liquid having been introduced into a phial or tube of known capacity, was diluted with distilled water, until it reached a particular mark upon the side, corresponding to 1000 water-grain measures ; care being taken of course to add previously a few drops of a solution of sulphocyanide of potassium. The depth of tint was then compared with that of the standard solutions before mentioned, contained in tubes or phials of similar diameter, in which certain known quantities of iron, ranging from the $\frac{1}{1000}$th to the $\frac{1}{4}$th of a grain, were contained in the same bulk of water. In order to render the comparison of tints more perfect, the tubes were placed against a sheet of white writing paper, and held between the eye and the diffused light. Operating in this way, the author was enabled to estimate the $\frac{1}{1000}$th of a grain of iron per gallon with the greatest readiness. It was sometimes found preferable to employ but one standard solution. The proportion of iron, in the liquid tested, was then determined by measuring the volume of water that was required to lighten the tint so as to render it identical with that of the normal solution, or *vice versâ*.

On Dr. Keller's* supposed formation of Metacetonic Acid from Flour and Leather. BY R. W. FORSTER.

A mixture of flour with scraps of leather, carbonate of lime, and water, having been digested for three weeks at a gentle heat, the liquid was strained off, the dissolved lime-salt converted into a soda-salt, the solution concentrated by evaporation, and distilled with excess of sulphuric acid. A portion of the acid distillate was then neutralized with carbonate of soda, the remainder added to it, and the whole distilled.   According to Keller, butyric ether should distil over, acetate and metacetonate of soda remaining in the retort. The distillate obtained by Mr. Forster, however, had an odour not at all resembling that of butyric ether; and the dry residue, when distilled with sulphuric acid, yielded a distillate which had not the odour of either acetic or metacetonic acid, and gave no odour of acetic ether when heated with alcohol and sulphuric acid. The liquid also yielded a baryta-salt containing 65·5 per cent (mean) of baryta, a quantity differing by 1½ per cent from 67·4, the amount required by the formiate; the deficiency was probably due to slight impurities. Acetate of baryta contains 60, and metacetonate of baryta 54·06 per cent of the base. Moreover, the solution of the baryta-salt rapidly reduced nitrate of silver. The principal constituent of the distillate appears therefore to be *formic acid.*

* See this Journal, Vol. III, p. 190.

PROCEEDINGS

MEETINGS OF THE CHEMICAL SOCIETY.

January 19, 1852.

Professor Daubeny, President, in the Chair.

The following donations were announced:

" Berattelse om Framstegen i Fysik," 1849: af E. Edlund.
" Ofversigt af Kongl. Vetenskaps-Akademiens Förhandlingar, 1850 from the Royal Stockholm Academy.
" Denkschriften der Kaiserlichen Akademie der Wissenschaften:" Zweiter Band.
" Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften," Band VI. Heft I—V: from the Imperial Academy of Vienna.

" Proceedings of the Glasgow Philosophical Society," Vol. III. No. 3: from the Society.
" Pharmaceutical Journal," Vol. II, No. 7: from the Editor.
" Journal of the Franklin Institute," Vol. XXII, No. 2: from the Institute.
" The Literary Gazette," Nos. 1823—1826: from the Publishers.
" Prideaux's Scale of Equivalents:" from Mr. Whipple.

The following papers were read:

1. " On the Analysis of the Water supplied by the Bristol Water-works Company:" by Thornton J. Herapath.
2. " On a quick approximative Method of Estimating minute quantities of Iron by means of a Colorimeter:" by the same.
3. " On the Decomposition of Citrate of Lime in contact with Putrefying Curd:" by Henry How.

Dr. Hofmann made a verbal communication on Liebig's new method of estimating the quantity of urea contained in urine. He stated that various methods had previously been recommended for estimating urea, among others, that of converting the urea into carbonate of ammonia, and ascertaining the quantity of nitrogen. This method, as well as some others, required delicate and careful manipulation; others again have been proved to furnish incorrect results. Professor Liebig had been often applied to by his physiological friends at Giessen, to devise some simple method of effecting this object, such as a medical man might himself readily apply; and he had succeeded in discovering a process which appeared to offer the means of estimating urea with great facility. It consists in treating the urine under examination with nitrate of red oxide of mercury. Urea combines with this substance, and forms a snow-white, almost insoluble, compound, which is immediately precipitated, when urine, or a fluid containing urea, is mixed with a solution of the nitrate of mercury containing no free acid. The precipitate contains one atom of urea, one atom of nitric acid, and four atoms of red oxide of mercury. As nitric acid is set free in the process, and as this free acid prevents the further action of the nitrate, it is necessary to neutralize the liquor after each addition of nitrate, with baryta-water. Liebig has found, however, that the presence of common salt in the urine presents a difficulty in the application of the process, which he has not yet completely got over.

February 2, 1852.

Dr. Lyon Playfair, Vice-President, in the Chair.

The following donations were announced:

" Smithsonian Contributions to Knowledge," Vol. II.

"Appendix I. to Vol. III. of the Smithsonian Contributions to Knowledge, containing an Ephemeris of the planet Neptune:" by Sears C. Walker.

"Report to the Smithsonian Institution on the History of the Discovery of Neptune:" by B. A. Gould, Jun.

" Fourth Annual Report of the Board of Regents of the Smithsonian Institution for 1849."

"Notices of Public Libraries in the United States of America:" by Charles C. Jowett: from the Smithsonian Institution.

"Reports from the Secretary of the Treasury, of scientific investigations relating to Sugar and Hydrometers, made under the superintendence of Professor A. D. Bache:" by Professor R. S. M‘Culloch : from the Author.

"Proceedings of the American Association for the Advancement of Science," in 1850 : from the Association.

"The American Journal of Science and Arts:" by Professor Silliman, No. 36, for Nov. 1851 : from the Editor.

"Journal of the Franklin Institute," Vol. XXIII, Nos. 3 and 4 : from the Institute.

"The Pharmaceutical Journal," Vol. III, No. 8 : from the Editor.

"The Literary Gazette," No. 1827 : from the Publishers.

"Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften," Band. VII, Heft 1 and 2 : from the Imperial Academy of Vienna.

"Stahl's Fundamenta Chymiæ :" from Mr. George Whipple.

"Six Medallions of foreign Philosophers :" from Mr. D. Boru.

The following papers were read :

1. "On a New Method of obtaining Hippuric Acid in considerable quantity without Evaporation of the Urine; and on some of its products of Decomposition :" by Edward Riley, Assistant in the Museum of Practical Geology.

2. "On Populin :" by M. Rafaelle Piria.

February 16, 1852.

PROFESSOR DAUBENY, President, in the Chair.

Frederic Claudet, Esq., of University College; Christopher Leefe Dresser, Esq., of Leeds; Charles B. Mansfield, B.A.; of Half-Moon Street; Joshua Hutchinson Robson, Esq., of 6, Highbury Park; and Rees Reece, Esq., of Ather Peat Works, near Dublin, were duly elected Fellows of the Society.

The President announced the names of the Vice-President and four other Members of the Council, who retire from office, and the Vice-President and four other Members of Council, together with the remaining Officers and Members of the present Council, who were proposed by the Council to be elected at the next General Meeting of the Society.

The following donations were announced:

" The American Journal of Science and Arts:" by Professor Silliman, for January 1852 : from the Editor.

" The Quarterly Journal of the Geological Society," for February 1852 : from the Society.

" The Literary Gazette," for January 31, and February 14: from the Publishers.

"Specimens of Zinc ores, in the natural and prepared states; Metallic Zinc, showing the hot and cold fractures; Rolled Zinc; a Mould illustrating the method of making Zinc Casts; a Cast of the Head of Sir Robert Peel:" from the Vieille Montagne Zinc Works.

"Specimens illustrating the Manufacture of Kelp and Iodine in Ireland :" from Mr. John Ward.

The following papers were read:

1. " On the Variation in the relative Proportion of Potash and Soda present in certain Samples of Barley grown in plots of ground artificially impregnated with one or other of these Alkalies :" by Dr. Daubeny, F.R.S.

2. " On the Compounds of Cotton with the Alkalies:" by J. H. Gladstone, Ph.D.

March 1, 1852.

Professor Graham in the Chair.

G. B. Buckton, Esq., of Gloucester Place, Hyde Park, was duly elected a Fellow of the Society.

The following donations were announced :

" The Pharmaceutical Journal," for March : from the Editor.

" The Literary Gazette," for February 28: from the Publishers.

"Specimens of Hippuric Acid in different states of purification; of Benzoic Acid prepared from Hippuric Acid; and of Glycocol in the pure and impure state :" from Mr. Edward Riley.

The following papers were read :

1. " On the occurrence of Capric and Caprylic Acids in some Fousel Oils :" by T. H. Rowney.

2. " On Dr. Keller's supposed formation of Metacetonic Acid from Flour and Leather :" by R. W. Forster.

March 15, 1852.

PROFESSOR DAUBENY, President, in the Chair.

The following donations were announced :

" The Literary Gazette," for March 6th and 13th : from the publishers.

" Experimental Researches in Electricity ;" Twenty-sixth series, " On Lines of Magnectic force, &c." by Michael Faraday, D.C.L., F.R.S. : from the author.

" On a Method of obtaining a perfect vacuum in the receiver of an Air-pump :" by Thomas Andrews, M.D., F.R.S.: from the author.

The following gentlemen were duly elected Fellows of the Society :

Alfred Smee, Esq., F.R.S., Finsbury Circus; Alfred Fletcher, Esq., Denmark Hill, Camberwell: James Higgin, Esq., Manchester.

The following papers were read :

1. " On the Detection of Alum in Flour, with remarks on the Preparation of Distilled Water and Pure Potash :" by J. H. Pepper.

2. " Contributions towards the History of Tannic Acid :" by Dr. Strecker.

Dr. Hofmann made some observations on Liebig's new process for estimating Urea, and described the methods which this Chemist uses for preparing his standard solution of mercury, and for estimating the amount of chloride of sodium in urine.

NOTICES

OF

PAPERS CONTAINED IN

British and Foreign Journals.

Chemical Report on the cause of the Fire in the 'Amazon.'

By Professor Graham.

February 17th, 1852.

My Lords,

In reply to the questions arising out of the disastrous loss of the 'Amazon' by fire which are proposed to me for a Chemical opinion, I beg to submit to your Lordships the following statements and conclusions.

The practice of mixing together the various stores of the engineer, consisting of oils, tallow, soft-soap, turpentine, cotton waste and tow, and placing them in heated store-rooms contiguous to the boilers, must be looked upon as dangerous in no ordinary degree, for several reasons. Although oil in bulk is not easily ignited, particularly when preserved in iron tanks, still when spilt upon wood or imbibed by tow and cotton waste, which expose much surface to air, the oil often oxidates and heats spontaneously, and is allowed to be one of the most frequent causes of accidental fires. The vegetable and drying oils used by painters are most liable to spontaneous ignition, but no kind of animal or vegetable oil or grease appears to be exempted from it; and instances could be given of olive-oil igniting upon sawdust; of greasy rags from butter, heaped together, taking fire within a period of twenty-four hours; of the spontaneous combustion of tape-measures, which are covered with an oil-varnish, when heaped together; and even of an oil-skin umbrella put aside in a damp state. The ignition of such materials has been often observed to be greatly favoured by a slight warmth, such as the heat of the sun. I am also informed by Mr. Braidwood, that the great proportion of fires at railway-stations have originated in the lamp-store, and that in coach-works also, when the fire can be traced, it is most frequently to the painters' department, the fire having arisen spontaneously from the ignition of oily matters. Lamp-black and ground charcoal are still more inflammable, when the smallest quan-

tity of oil obtains access to them, and should not be admitted at all among ships' stores.

· The stowing metallic cans or stoneware jars of either oil or turpentine in a warm place is also attended with a danger which is less obvious, namely, the starting of the corks of the vessels, or the actual bursting of them by the great expansion of the liquid oil which is caused by heat. These liquids expand in volume so much as one, upon thirty by a rise of not more than 60° of temperature, or by such a change as from the ordinary low temperature of 40° to a blood-heat; the latter temperature may easily be exceeded in an engine-room. It is remarkable that the burning a few years ago of a large steamer on the American lakes, which even surpassed in its fatality the loss of the 'Amazon,' was occasioned by the bursting, in the manner described, of a jar of turpentine placed upon deck too close to the funnel, by a party of journeymen painters who were passengers. This steamer was also on her first voyage, and being newly varnished, the flames spread over her bulwarks and extended the whole length of the vessel in a few minutes.

The bulkheads of coal-holds appear to admit of obtaining considerable security from fire by being constructed double where close to the boiler, with a sheet of air between the two partitions. The tendency of coals to spontaneous ignition is increased by a modera e heat, such as that of the engine-room, from which they would be protected by the double partition. I have obtained instances where coals took fire in a factory, on two different occasions, by being heaped for a length of time against a heated wall, of which the temperature could be supported by the hand; also of coals igniting after some days upon stone flags covering a flue, of which the temperature was not known to rise above 150°, and of coals showing indications of taking fire by being thrown in bulk over a steam pipe. These were Lancashire coals, which are highly sulphureous; but the same accident occurred with Wallsend coals, at the Chartered East Company's works in London, where the coals were twice ignited through a two-feet brick wall, of which the temperature was believed by Mr. Croll not to exceed 120° or 140°.

The surface of deal in the partition opposed to the boiler would probably be better protected from fire by impregnating the wood with a saline solution, which diminishes combustibility, such as the zinc solution of Sir W. Burnett, rather than by coating the wood on the side next the boiler with sheet iron. Indeed, this use of iron appears to introduce a new danger. The iron being a good conductor of heat, the wood below is heated nearly as much as if uncovered, and wood in contact with iron appears to be brought by repeated heating to an extraordinary degree of combustibility, and to become peculiarly liable to spontaneous ignition.

Mr. Braidwood, who has been led to that conclusion, gave an

instance of wood covered by sheet iron igniting spontaneously in a wadding manufactory. The numerous occasions, also, on which wood and paper have been ignited by Perkins' heated water-pipes, equally exemplify the dangerous consequences which may arise from moderately heated iron in long contact with combustible matter.

The most obvious precautions for guarding against the spontaneous ignition of coal stowed in ships' bunkers appear to be the taking the coal on board in as dry a condition as possible, and the turning it over, if there is room for doing so, as soon as the first symptom of heating is perceived. An obnoxious vapour is described as always preceding the breaking out of the fire, and affords warning of the danger. The ignition of Newcastle coals in store is not an unfrequent occurrence at the London gas-works. It appears always to begin at a single spot, and is met by cutting down upon and removing at once the heated coals. Long iron rods are placed upright in the coal heap, which can be pulled out, and indicate by their warmth the exact situation of the fire. Steam can be of little avail for extinguishing fire among coals in bulk; and water, although it may extinguish the fire for the time, is too apt to induce a recurrence of the evil.

For extinguishing a fire occurring in berths or cabins in the immediate vicinity of the boiler and engine-room, steam might be more advantageously applied, means of turning on the steam being provided upon the upper deck, or other distant place of safety. Steam, however, can only be said to be efficient in extinguishing flame, or a blaze from light objects, and is not to be relied upon beyond an early stage of a fire. Upon a mass of red-hot cinders the extinguishing effect of steam is insensible.

An essential condition of applying steam with success to the extinction of a fire in the engine-room, would be to prevent the rapid ingress and circulation of air at the same time, which is occasioned by the draught of the fires. This could only be done completely by valving the chimneys : for the quantity of heated air passing off by the funnels greatly exceeds in volume the steam produced by the boilers in the same time, and would rapidly convey away the steam thrown into the atmosphere of the engine-room, and prevent any possible advantage from it.

The fire in the 'Amazon' appeared to the witnesses to take its rise either in the small oil store-room situated over the boiler, or in a narrow space of from three to eleven inches in width between a bulkhead and the side of the boiler, immediately under the same store-room. No substance remarkable for spontaneous ignition, such as oiled cotton waste, was actually observed in the store-room or the space referred to. The wood itself of the bulkhead, which was within a few inches of the boiler, may have been highly dried and sensibly heated by its proximity to the latter, but is not likely to have acquired

any tendency to spontaneous ignition ; for when that property results from low heating, it is an effect of time, requiring weeks or months to develop it. The same observation applies to the decks in contact with the steam-chest which incased the base of the funnel.

Nor does it appear probable that the coals in the coal-hold of the vessel gave occasion to the fire by heating of themselves, and then burning through the wooden partition of the oil-store with which they were in contact.

These coals were from Wales, and not remarkable for this property.

They are also said to have been shipped in a dry and dusty state, and not damp, a month or two previously.

Their ignition would also have been preceded by the strong odour before referred to, which does not appear to have been remarked, although the coal-hold communicated directly with the boiler-room.

Oil was seen to drop from the floor of the store-room upon the top of the boiler, but not in greater quantity than might be accidentally spilt in drawing the oil from the tank for the use of the engineers.

A parcel of twenty-five newly-tarred coal-sacks, which had been thrown upon the boiler, also obtained, it is supposed, some of the same oil. This oil appears to be the matter most liable to the possibility of spontaneous ignition, which was noticed near the spot where the fire commenced.

But the sudden and powerful burst of flame from the store-room, which occurred at the very outset of the conflagration, suggests strongly the intervention of a *volatile* combustible, such as turpentine, although the presence of a tin can of that substance in the store-room appears to be left uncertain. It was stated to be there by two witnesses, but its presence is denied by a third witness. I find upon trial, that the vapour given off by oil of turpentine is sufficiently dense, at a temperature somewhat below 110°, to make air explosive upon the approach of a light. Any escape of turpentine from the heated store-room would therefore endanger a spread of flame, by the vapour communicating with the lamps burning at the time in the boiler-room, or even with the fire of the furnaces.

The fire appears not to have begun in the tarred sacks lying upon the boiler, although from their position, which was close to the store-room, they must have been very early involved in the conflagration, and contributed materially to its intensity. The sacks appear to have been charged each with about two pounds of tar, thus furnishing together fifty pounds of that substance, in a condition the most favourable that can be imagined for rapid combustion. The freshness of the tar and its high temperature would make it ignite by the least spark of flame, although not prone to spontaneous ignition. The burning of a group of newly-tarred cottages

in Deptford, which came under the notice of Mr. Braidwood, arose
from their being set on fire by lightning, while the sun was shining
upon them, and the tar liquefied by the heat.

The origin of the fire must remain, I believe, a subject of specula-
tion and conjecture; but the extreme intensity and fearfully rapid
spread of the combustion are circumstances of scarcely inferior inte-
rest, which are not involved in the same obscurity.

The timber of the bulkheads and decks near the engine-room is
reported to have been of Dantzic red wood or Riga pine, and such
was the character of a portion of the Amazon's timber which was
supplied to me for chemical examination. The wood has had its
turpentine drawn off, and differs in that respect from pitch pine.
The Dantzic red wood is, in consequence, less combustible than pitch
pine, but more porous and spongy. Oil-paint is absorbed, and dries
more quickly upon this porous wood than upon oak and other dense
woods. After their paint is well dried, pine and other woods
certainly acquire from it some protection from the action of feeble
and transient flames, which might kindle the naked wood. But
the effect of paint, especially of fresh paint, appears to be quite
the reverse, when the wood is exposed to a strong although merely
passing burst of flame. The paint melts and emits an oily vapour
which nourishes the flame, and soon fixes it upon the wood. There
can be no doubt, therefore, that the timber of the 'Amazon' was
in a more inflammable state than ship-timber usually is, from being
recently painted, and also probably from its newness and compara-
tive dryness.

But the circumstance which appears above all others to give a
character to the fire in the 'Amazon' was its occurrence, not in a
close hold or cabin, but in a compartment of the vessel where a
vigorous circulation of air is maintained by the action of the boiler-
fires and their chimneys. The air of the engine-room must be
renewed under this influence every few minutes, and would be so
although full of flames rising above deck through the hatchways;
for a portion of these flames would always escape by the funnels,
and add to their aspirating power instead of diminishing it. The
combustion of bulkheads or decks once commenced in this situation
would therefore be fanned into activity and powerfully supported.

The destruction of the floor of the oil store-room, and the over-
turning, in consequence, of the oil-tanks and combustibles into the
well of the boiler-room, was probably the crisis of the fire. A mass
of combustible vapour would speedily be generated, and shot about
on all sides, of which the kindling power upon the new and painted
timber of the bulkheads and decks would be wholly irresistible.

The burning of the 'Amazon' impresses most emphatically the
dangerous and uncontrollable character of a fire arising in the engine
or boiler room, where the combustion is animated by a steady and

powerful circulation of air, and the danger of collecting combustible matter together in such a place. The removal of the oil stores to a safer locality is, fortunately, generally practicable, and is the measure best calculated to prevent the recurrence of any similar catastrophe.

I have the honour to remain, &c., &c.

THOS. GRAHAM.

To the Lords of the Committee of
    Privy Council for Trade.

Contributions to the knowledge of the Manufacture of Gas.
By E. Frankland, Ph.D.

(Read before the Manchester Literary and Philosophical Society, January 13, 1852.)

(ABSTRACTED BY THE AUTHOR.)

The constituents of purified gas, as used for illuminating purposes, are hydrogen, light carburetted hydrogen, carbonic oxide, olefiant and other gases having the general formula $C_n H_n$, the vapours of hydrocarbons of the form $C_n H_{n-6}$, and other hydrocarbons, the formulæ of which are unknown; in addition to these, coal-gas usually contains small quantities of nitrogen, oxygen, and bisulphide of carbon vapour; but these, for our present purpose, may be entirely disregarded.

It has always been asserted, that hydrogen and carbonic oxide possess no illuminating power, and that the light emitted by coal-gas is due to light carburetted hydrogen, olefiant gas, and other hydrocarbons; I hope, however, to prove, by the experiments detailed below, that light carburetted hydrogen is, for all practical purposes, also entirely devoid of illuminating power; and that therefore the whole of the light giving effect is due to the olefiant gas and hydrocarbons. This is an important point, as we shall find that it much simplifies the estimation of the illuminating power of any gas, and teaches us that the nature of the combustible diluents of the olefiant gas and hydrocarbons has no effect whatever upon the quantity of light emitted by the mixture.

The constituents of coal-gas may therefore be divided into two classes, viz., illuminating and non-illuminating constituents. To the first will belong olefiant gas and the other hydrocarbons above-mentioned; and to the second, hydrogen, light carburetted hydrogen, and carbonic oxide. To the first class alone the illuminating power of the gas is due; but one member at least of the second class is also indispensable as a diluent, without which we should find great difficulty in consuming the hydrocarbons without the production of much smoke. The members of the first class are all decomposed at a white heat instantaneously, at a red heat more slowly, depositing the whole, or the greater part of their carbon in the form of very fine particles, which become so many centres for the radiation of light in a

gas flame; and the greater the number of particles existing in a flame at the same time, the greater will be the light emitted by that flame. It is therefore evident, that the value of these hydrocarbons for the production of light, depends directly upon the quantity of carbon contained in a given volume, and is altogether independent of the hydrogen with which this carbon is combined; consequently, the densest or most easily condensible of these gases and vapours of the first class are those which possess the highest illuminating power. All the compounds belonging to this class are, as before stated, decomposed more or less rapidly at a red heat; in the ordinary process of gas-making, the interior walls of the retorts soon become coated with a stratum of carbon derived from this source. Now the extent of this decomposition must depend, first upon the length of time during which they are exposed to the heated materials, and secondly upon the number of particles which are in contact with the red-hot surface; consequently, it will be diminished, first, by removing the gases rapidly from the retort, and secondly, by the mixture of the illuminating constituents with the non-illuminating ones: for it is evident, that the number of particles of olefiant gas in contact with a given surface, would only be half so great if this gas were diluted with an equal volume of hydrogen, as it would be without such an admixture. Besides the use of the second class, or non-illuminating gases, which has been already stated, they are of value as forming a medium for the solution of the vapours of such hydrocarbons as exist in the liquid or even solid state, at the ordinary temperature of the atmosphere; and they thus enable us to convert an additional quantity of illuminating materials into the gaseous form, which they retain permanently unless the temperature fall below the point of saturation. The gain in illuminating power which is thus obtained, will be perhaps better seen from the following example. If 100 cub. in. of olefiant gas, being allowed to saturate itself with the vapour of a volatile hydrocarbon containing three times the amount of carbon in a given volume of its vapour as that contained in an equal volume of olefiant gas, took up, or dissolved in this way 3 cub. in. of hydrocarbon vapour, then, if we express the value in illuminating power of 1 cub. in. of olefiant gas as unity, the illuminating power of the 103 cub. in. of the mixture of olefiant gas and hydrocarbon vapour will be 109; now, if we mix these 103 cub. in. with 100 cub. in. of hydrogen, the mixture will be able to take up an additional 3 cub. in. of the hydrocarbon vapour, and the illuminating power of the 206 cub. in. will then become 118. Thus the hydrogen produces a gain in illuminating power equal to 9 cub. in. of olefiant gas, or nearly 4·5 per cent upon the total volume of mixed gases. When we consider that coal-naphtha contains hydrocarbons of great volatility, and which are no doubt the surplus remaining after the saturation of the gas from which

they have condensed, the importance of this function of the non-illuminating class of combustible gases will be sufficiently evident. I may here remark, that incombustible gases could not be employed for this purpose, since their cooling influence upon the flame during the subsequent burning of the gas would diminish the light to a far greater extent than the hydrocarbon vapour could increase it. It is evident, that all the three non-illuminating gases forming the second class, would perform both the offices I have assigned to them equally well; and therefore we have as yet seen no reason for giving our preference in favour of any one of these diluents. If, however, we study their behaviour during combustion, we shall find, that where the gas is to be used for illuminating purposes, hydrogen has qualities which give it a very decided preference over the other two. When gas is used for lighting the interior of public buildings and private houses, it is very desirable that it should deteriorate the air as little as practicable, or in other words, it should consume as small a quantity of oxygen, and generate as little carbonic acid as possible; the oppressive heat which is often felt in apartments lighted with gas also exemplifies the great advantage of its generating a minimum amount of heat.

1 cub. ft. of light carburetted hydrogen at 60° F., and 30 in. Bar., consumes 2 cub. ft. of oxygen during its combustion, and generates 1 cub. ft. of carbonic acid, yielding a quantity of heat capable of heating 5 lbs. 14 oz. water from 32° to 212°.

1 cub. ft. of carbonic oxide consumes $\frac{1}{2}$ a cub. ft. of oxygen, generates 1 cub. ft. of carbonic acid, and affords heat capable of raising the temperature of 1 lb. 14 oz. of water from 32° to 212°.

1 cub. ft. of hydrogen consumes $\frac{1}{2}$ a cub. ft. of oxygen, generates no carbonic acid, and yields heat capable of raising the temperature of only 1 lb. 13 oz. water from 32° to 212°.

Thus, light carburetted hydrogen is very objectionable as a diluent, not only on account of the carbonic acid which it generates, and the large quantity of oxygen it consumes, but also by reason of the very great amount of heat, which in relation to its volume it evolves on combustion, the absolute thermal effect being more than three times as great as that of either of the other gases. The quantity of heat evolved by the combustion of equal volumes of carbonic oxide and hydrogen is nearly, and the amount of oxygen consumed, quite the same, but the quantity of carbonic acid evolved by the first gives a decided preference to hydrogen as the best diluent.

The same comparison also shows, that where the gas is to be used for heating purposes, and the products of combustion are carried away, light carburetted hydrogen is by far the best diluent.

The experiments of Dulong on the absolute thermal effect of

hydrogen, light carburetted hydrogen, and carbonic oxide are taken as the basis of the foregoing calculations.

These remarks indicate the objects that should be chiefly regarded in the generating department of the manufacture of gas for illuminating purposes : these are

1. The formation of a due proportion of illuminating and non-illuminating constituents, so that on the one hand, the combustion of the gas shall be perfect, and without the production of smoke or unpleasant odour, and on the other, the volume of gas required to produce a certain amount of light shall not be too great.

2. The extraction of the largest possible amount of gaseous illuminating compounds from a given weight of material.

3. The presence of the largest possible proportion of hydrogen amongst the non-illuminating constituents, to the exclusion of light carburetted hydrogen and carbonic oxide, so as to produce the least amount of atmospheric deterioration in the apartments in which the gas is consumed.

I have not introduced these preliminary observations to show the inductive reasoning by which the process of gas-making described below was arrived at, for, I believe that, so far as these considerations are concerned, that process was accidentally adopted; but I bring them forward to illustrate and explain the principles involved in it, and also to show that a close study of the chemistry of gas-manufacture would have led to the discovery of this more philosophical method of gas-generation long ago.

Various attempts have been made to estimate the illuminating power of coal and other gases from the analytical results they yield, but hitherto no certain method of accomplishing this has been established.   Dr. Henry regarded, and not unjustly, the consumption of oxygen by a given volume of gas to be a rough estimation of its illuminating power; but it is evident, that although generally those gases which have the highest illuminating power consume most oxygen, yet this is not always the case ; for a gas containing 10 per cent of olefiant gas, 20 per cent of light carburetted hydrogen, and 70 per cent of hydrogen, would consume much less oxygen during combustion, than one containing only 5 per cent of olefiant gas, and in which the proportion of light carburetted hydrogen and hydrogen were reversed, although its illuminating power would be twice as great.

It will be seen from what has been already said respecting the illuminating power of carbo-hydrogens, that the more dense these are, the greater does that illuminating power become.   This important fact was first pointed out in reference to coal-gas, by Mr. Leigh,*

* Memoirs of the Manchester Lit. and Philosoph. Soc., IX. (new series), 303.

who was also the first to make an approach towards estimating the illuminating power of gas from its analysis.   Mr. Leigh regards the illuminating power of coal-gas as due to light carburetted hydrogen, olefiant gas, and hydrocarbons, and that the value of the latter is directly proportional to the quantity of oxygen required for their combustion.   If we leave the light carburetted hydrogen entirely out of the calculation, as I shall prove that this gas has practically no illuminating power, this method generally gives results not far from the truth, but which are nevertheless liable to very considerable error, from the fact that the amount of oxygen consumed does not depend alone upon the luminiferous ingredients of the carbon, but also upon the amount of hydrogen combined with that element, and which is necessarily a variable quantity, being in some of the hydrocarbons in the proportion, $C : H = n : n$; in others, $C : H = n : n - 6$; and in others even, $C : H = n : n - 10$.   If, however, we estimate the volume of carbon vapour contained in the luminiferous hydrocarbons, and make that the basis of our calculation, we avoid this source of error, and obtain a correct expression for the illuminating power, however much the composition of the hydrocarbons may vary.   I have already pointed out a method for accomplishing this ;* and Mr. Leigh, in the memoir to which I have already alluded, also describes a similar plan which he employs for the determination of the consumption of oxygen by these bodies.

The method which I have adopted in the annexed experiments is the following :

A known quantity of the gas previous to the action of sulphuric acid is exploded with an excess of oxygen, and the volume of carbonic acid produced accurately noted.   Another known volume of the same gas, after the withdrawal of the hydrocarbons by sulphuric acid, is then similarly exploded with oxygen, and the carbonic acid formed also estimated.   Thus the percentage amount of hydrocarbons, plus the volume generated by the non-luminous gases alone, being known, it is easy to calculate the amount of carbonic acid generated by 1 volume of the hydrocarbons.   Thus if we designate the percentage of hydrocarbons absorbed by sulphuric acid, by A, the volume of carbonic acid generated by 100 volumes of the original gas, by B, the carbonic acid formed by the residual gas after absorption of hydrocarbons, by C, and the volume of carbonic acid generated by the combustion of 1 volume of the hydrocarbons alone by X, we have the following equation :

$$X = C - B$$

and therefore the amount of carbonic acid generated by 1 volume of the hydrocarbons is represented by

$$\frac{C - B}{A}$$

* Chem. Soc. Qu. J., II., 275.

but as one volume of carbon vapour generates one volume of carbonic acid, this formula also expresses the quantity of carbon vapour in 1 volume of the luminiferous constituents.

For the purpose of comparison, however, I represent the value of these hydrocarbons in their equivalent volume of olefiant gas, one volume of which contains 2 volumes of carbon vapour; for this purpose, the last expression need only be changed to

$$\frac{C-B}{2A}$$

Thus, if a gas contains 10 per cent of hydrocarbons, of which, one volume contains 3 volumes of carbon vapour, the quantity of olefiant gas to which this 10 per cent is equivalent, will be 15.

The illuminating power of the coal gases mentioned below has also been practically tested by Bunsen's photometer, and the results are corrected to those which would have been obtained by using a sperm candle, burning 120 grs. per hour; and one of these candles, burning for ten hours, is taken as the standard of comparison for the total quantity of light yielded by a given volume of gas; thus, when it is stated that the total quantity of gas produced from 1 ton of coal is equal to 4816 candles, it is intended that the light afforded by the gas is equal to that yielded by 4816 sperm candles, each burning 10 hours, and at the rate of 120 grs. per hour.

The following experiments, which I lately made at the request of two merchants of this town, upon a new process of gas-making, known as White's hydrocarbon process, serve to illustrate the principles laid down in the preceding pages.

Mr. White's process consists essentially in the generation of non-illuminating combustible gases by the action of steam upon charcoal, coke, or other substances, in a separate retort, and the introduction of these gases, along with an excess of watery vapour, into the retort in which the illuminating gases are being generated, and in such a manner, that these latter gases shall be swept out of the retort as rapidly as possible, and removed from the destructive influence of a high temperature. The excess of steam accompanying the water-gases into the second retort, performs there a remarkable office; it reacts upon the tar and fuliginous matter in a manner that will be described below, and gives rise to the formation of a great additional quantity of gas, a very large proportion of which is pure hydrogen. That this reaction of the steam should be confined entirely to the tar and other refuse matters, and should not affect the luminiferous gases generated in the same retort is scarcely conceivable, since the constitution of tar and gaseous hydrocarbons is so nearly alike; yet any destruction of illuminating principles that may be thus caused, is immensely overbalanced by the quantity of these principles, which are saved from decomposition by their rapid removal

from the influence of a high temperature, and by the vapours of volatile hydrocarbons with which the water-gases remain more or less saturated.

WHITE'S PROCESS APPLIED TO RESIN.

I. PRACTICAL RESULTS.

	1st Exp.	2nd Exp.	3rd Exp.	4th Exp.	Average.
Gas produced per ton of resin . . .	26000 cbc. ft.	28120 cbc. ft.	36820 cbc. ft.	29300 cbc. ft.	30060 cbc. ft.
Resin-oil produced per ton of resin . .	88·9 galls.	64 galls.	41·8 galls.	84·8 galls.	69·9 galls.
Coal consumed in heating retorts . .	1396 lbs.	1396 lbs.	1399 lbs.	1406 lbs.	1399 lbs.
Charcoal for water-gas	83 ,,	100 ,,	111 ,,	97 ,,	98 ,,
Water used . .	606 ,,	639 ,,	790 ,,	606 ,,	660 ,,

II. ANALYTICAL RESULTS.

PERCENTAGE COMPOSITION OF PURIFIED GASES.

	1st Exp.	2nd Exp.	3rd Exp.	4th Exp.	Average.
Olefiant gas and hydrocarbons . .	8·27	7·94	7·78	8·53	8·13
Light carburetted hydrogen . .	18·76	45·06	22·79	32·25	29·71
Hydrogen	42·03	37·59	50·27	43·62	43·38
Carbonic oxide	30·93	9·41	19·16	15·60	18·78
	100·00	100·00	100·00	100·00	100·00

ILLUMINATING VALUE OF OLEFIANT GAS AND HYDROCARBONS EXPRESSED IN EQUIVALENT QUANTITY OF OLEFIANT GAS.

1st. Experiment.	2nd Experiment.	3rd Experiment.	4th Experiment.	Average.
11·58 per cent.	11·11 per cent.	10·89 per cent.	11·94 per cent.	11·38 per cent.

WHITE'S PROCESS APPLIED TO COALS AND CANNELS.

In order to obtain a fair comparison of the results yielded by the various coals when distilled alone (as in the usual process of gas-making) with those obtained from the same coals when treated with water-gas according to the hydrocarbon process, each coal was distilled first by itself, and then with the addition of water-gas, equal weights being used for each experiment.

I. PRACTICAL RESULTS.

Name of coal.	Cubic feet of gas per ton.		Illuminating power per ton in sperm candles.		Gain per ton by White's process.		Gain per cent by White's process.	
	By old process.	By White's process.	By old process.	By White's process	Quantity of gas in cubic feet.	Illuminating power in sperm candles.	Quantity of gas.	Illuminating power.
Wigan cannel (Ince Hall) . . .	10,900	16,120	4,816	6,448	5,220	1,632	47·9	33·9
Wigan ditto (Balcarres). . .	10,440	15,500	4,156	5,920	5,060	1,764	48·5	42·4
Boghead cannel . .	13,240	38,160	11,340	21,368	24,920	10,028	178·2	88·4
Ditto, 2nd exp. .	....	51,720	....	20,688	38,480	9,378	290·6	82·4
Lesmahago cannel .	10,620	29,180	7,620	13,934	18,560	6,314	174·8	82·8
Methyl cannel .	9,560	26,400	5,316	11,088	16,840	5,772	176·2	108·6

QUANTITY OF COAL OR CANNEL REQUISITE FOR PRODUCING LIGHT EQUAL TO 1000 SPERM CANDLES, EACH BURNING TEN HOURS, AT THE RATE OF 120 GRS. PER HOUR.

Name of coal.	Weight of coal.	
	By old process.	By White's process.
Wigan cannel (Ince Hall) . . .	465·1 lbs.	347·4 lbs.
Wigan cannel (Balcarres) . . .	539·0 „	378·4 „
Boghead cannel	197·5 „	104·8 „
Lesmahago cannel	293·9 „	160·7 „
Methyl cannel	443·9 „	396·7 „
Newcastle coal (Pelton) . . .	745·7 „	

II. ANALYTICAL RESULTS.

PERCENTAGE COMPOSITION OF GASES.

	Wigan cannel (Ince Hall).		Boghead cannel.		Lesmahago cannel.		Methyl cannel.		Pelton coal.
	By old process.	By new process	By old process.	By new process.	By old process.	By new process.	By old process.	By new process.	By old process.
Hydrocarbons and olefiant gas . .	10·81	10·55	24·50	14·12	16·31	10·89	14·48	11·06	3·87
Light carburetted hydrogen . .	41·99	27·20	58·38	22·25	42·01	18·94	38·75	22·89	32·87
Hydrogen . . .	35·94	47·39	10·54	45·51	26·84	55 09	33·32	45 58	50·05
Carbonic oxide .	10 07	14·86	6·58	14·34	14·18	15·02	13·40	20 44	12·89
Carbonic acid . .	1·19	0·00	0·00	3·78	·66	·06	·05	·03	·32
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

ILLUMINATING VALUE OF OLEFIANT GAS AND HYDROCARBONS EXPRESSED IN EQUIVALENT QUANTITY OF OLEFIANT GAS.

Wigan cannel, by old process.	Wigan cannel, by new process.	Boghead cannel, by old process.	Boghead cannel, by new process.	Lesmahago cannel, by old process.	Lesmahago cannel, by new process.	Methyl cannel, by old process.	Methyl cannel, by new process.	Pelton coal, by old process.
per cent. 16·13	per cent. 13·72	per cent. 31·11	per cent. 19·84	per cent. 28·30	per cent. 19·05	per cent. 18·53	per cent. 14·04	per cent. 7·16

The foregoing results bring to light several circumstances highly favourable to the hydrocarbon process of gas-making, which could scarcely have been predicted previous to the actual trials being made. The first, and most important of these, is the disappearance of the carbonic acid contained in the water-gas, during its passage through the coal retort; this disappearance is so complete, that the resulting gaseous mixture actually contains a much smaller percentage than does the gas obtained by the distillation of the coal alone. There is little doubt that this removal of the carbonic acid depends upon its conversion into carbonic oxide by the carbonaceous matters in the coal retort; and of these, the coke is probably the most active, since the volatile matters do not differ materially from those produced during the distillation of resin; and these we have seen fail to remove the acid gas.

Another favourable circumstance occurring in the process, consists in the relatively small quantity of carbonic oxide that is produced. A large proportion of this gas would be equally objectionable with a high percentage of light carburetted hydrogen, on account of the quantity of carbonic acid formed during its subsequent combustion. A reference to the composition of the foregoing gases shows us, however, that in all cases, the amount of carbonic acid generated is less than that formed by the combustion of an equal volume of the gas obtained from the same coals by the ordinary process of manufacture, and in some cases it is even less than that produced by a pure coal-gas-flame giving an equal light. The favourable position which the hydrocarbon gases occupy in the above comparison, would not have been attained, if the whole, or even a very large portion of the water-gas had been generated in the charcoal retort; for when water-gas alone is generated, it is found to consist of hydrogen and carbonic oxide mixed with quantities of carbonic acid, varying from 0 to 15 per cent, according to the heat employed and other circumstances. When the percentage of the acid-gas is 0, then the volumes of hydrogen and carbonic oxide are equal; and as no important quantity of carbonic acid was ultimately present in the gases produced in the foregoing experiments, the whole of that gas entering the coal retort must be converted into carbonic oxide, and therefore we may consider the water-gas entering the coal retort as being composed of equal volumes of hydrogen and carbonic oxide. Now, if the increase in the total quantity of gas produced by the application of the hydrocarbon process to any given coal or cannel, were due only to the water-gas formed in the charcoal retort, it is obvious that the gain in carbonic oxide ought to be equal to the gain in hydrogen; but a glance at the analytical results shows that this is far from being the case. Thus, for instance, with Boghead gas, the proportion is

$$\text{Gain in H} : \text{gain in CO} = 3 \cdot 5 : 1$$

and with Lesmahago cannel,

<p style="text-align:center">Gain in H : gain in $CO = 4 \cdot 6 : 1$</p>

It is therefore evident that a large quantity of water-gas must be generated by the action of steam upon the carbonaceous materials in the coal retort, and that this water-gas contains a very much greater percentage of hydrogen than that produced in the charcoal retort. Although we are not yet sufficiently acquainted with the action of watery vapour upon organic substances at high temperatures, to state positively the cause of this excess of hydrogen, yet there can be little doubt that it is derived from the action of steam upon the hydro-carbor.₃ of the tar. For, as watery vapour in acting upon carbon transfers its oxygen to that element, forming carbonic oxide and an equal volume of hydrogen, so also when steam acts upon a compound of carbon and hydrogen, it produces carbonic oxide, but in doing so, sets at liberty not only its own hydrogen, but that of the carbo-hydrogen also; and thus the volumes of hydrogen and carbonic oxide remain no longer equal, but the volume of the former becomes double, treble, or even fourfold that of the latter.

An important feature in the history of a gas for illuminating purposes, is its behaviour when exposed to cold. I have therefore submitted several of the above gases to a temperature of 32°, and carefully ascertained the loss of volume by liquefaction of hydrocarbons. These experiments, as might be expected, show that the gases made by the new process, suffer less loss by this refrigeration than those made from the same material by the old process.

Name of gas.	Cubic feet of hydrocarbons condensed from 100 cubic feet of gas, on exposure to a cold of 32° F.
Boghead, by old process	4·42 cubic feet
Ditto by new process	·24 „
Methyl, by old process	·33 „
Ditto by new process	·07 „
Ince Hall, by old process	·37 „

The percentage amount of olefiant gas contained in the Pelton gas, and the gases of the Great Central and City of London Companies, would lead us to infer that their illuminating power is much lower than is really the case; for, according to the experiments upon cannel gases, it appears that when a consumption of 5 feet per hour produces a light equal to twenty candles, the gas contains 13·72 per cent of olefiant gas, or its equivalent in richer hydrocarbons; and, hence, we should expect that a gas containing only half this amount, would, when burnt at the same rate, produce a light equal only to ten candles, instead of thirteen, as is found to be the case. This excess of illuminating power in the case of *coal* gases over that indicated by analysis, is probably owing to the presence of luminiferous

constituents not condensible either by fuming sulphuric acid, or by chlorine; the nature of these constituents, and the cause why they cannot be detected by our present methods of gas analysis, I have already pointed out.* The following table exhibits this difference between the value of olefiant gas in coal-gas, compared with that in cannel-gas, and shows also, that in the case of the latter, the illuminating power is always directly proportional to the amount of olefiant gas to which the percentage of condensible hydrocarbons is equivalent. The establishment of this rule, with regard to gases having such different percentages of light carburetted hydrogen as the Boghead gas, with and without water-gas, I hold to be conclusive evidence that light carburetted hydrogen has no higher illuminating power than hydrogen or carbonic oxide.

Value of 1 cub. ft. of the olefiant gas, contained in the following gases, expressed in sperm candles, each burning ten hours, at the rate of 120 grs. per hour.

CANNEL GASES.

	Candles.
Ince Hall cannel	2·95
„ with water-gas . .	2·96
Boghead cannel	2·80
„ with water-gas . .	2·86
Lesmahago cannel	2·58
„ with water-gas . .	2·54
Ramsay's Newcastle cannel . . .	2·88
„ with water-gas . .	2·86
Methyl cannel	3·04
„ with water-gas . .	3·03

COAL GASES.

	Candles.
Pelton coal	4·23
City Company's gas (coal) . . .	3·73
Great Central Company's gas (coal) .	3·91

In conclusion, the advantages resulting from the application of Mr. White's hydrocarbon process to coals and cannels may be thus summed up:

1. It greatly increases the produce in gas from a given weight of coal or cannel, the increase being from 46 to 290 per cent, according to the nature of the material operated upon.

2. It greatly increases the total illuminating power afforded by a given weight of coal, the increase amounting to from 12 to 108 per

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* Chem. Soc. Qu. J. III, 42.

cent, being greatest when coals affording highly illuminating gases are used.

3. It diminishes the quantity of tar formed, by converting a portion of it into gases possessing a considerable illuminating power.

4. It enables us profitably to reduce the illuminating power of the gases produced from such materials as Boghead and Lesmahago cannels, &c., so as to fit them for burning without smoke and loss of light.

5. In addition to these positive advantages, the use of this process does not incur any additional expense in the working of the apparatus, the wear and tear of retorts, or the purification of the gas; and beyond a change of retorts, it involves no alterations in the construction of furnaces and apparatus at present employed in gas manufactories conducted on the old system.

On the Products of the destructive distillation of Animal Substances, Part II.

By Thomas Anderson, M.D., F.R.S.E.*

(ABSTRACTED BY THE AUTHOR.)

In a former paper on this subject, I announced the discovery, among the products of the destructive distillation of animal substances, of picoline, and described one new base to which I gave the name of petinine, and indicated the existence of several others. In examining these substances, I found that the quantity of material, though obtained from 300 pounds of bone oil, was much too small to admit of satisfactory results; the process was therefore repeated with a similar quantity of the oil, but I was again foiled by deficiency of material. The experience obtained in these preparations having enabled me to see that success could only be obtained by the use of very large quantities, I once more commenced the tedious preparation of the bases from no less than 250 gallons of the crude bone-oil.

The oil was rectified in a large cast-iron retort, furnished with a good condenser, kept cold by a current of ice-cold water. A gentle heat was applied, and the first 20 gallons, which consisted of equal bulks of a very volatile oil and water, charged with sulphide of ammonium, carbonate, and hydrocyanate of ammonia, were collected apart, and the rest of the oil received in a succession of casks which were numbered as they were filled. The watery fluid was separated from the oil, supersaturated with sulphuric acid, and boiled for a considerable time in a large copper boiler. It was then allowed to

cool, slaked lime added in excess, a copper head and condenser attached, and heat again applied. The distillate was collected in a large glass receiver, connected by a doubly bent tube with a second, containing hydrochloric acid, for the purpose of condensing ammonia and any of the very volatile bases which might be carried along with it. The distillate, which had a powerfully ammoniacal and putrid odour, was treated with sticks of caustic potash, which caused ammonia to escape with effervescence, while a small quantity of volatile bases collected on the surface, which were separated and preserved.

The oil, of which only the more volatile half was used, was agitated with dilute sulphuric acid. After two or three days, during which the agitation was frequently repeated, more water was added and the solution drawn off. The fluid, after the addition of more acid, was then boiled for the separation of Runge's pyrrol.

In my previous experiments, I had neglected this substance, but observing now that a very powerful odour was evolved when the fluid began to boil, the head of the boiler was attached for the purpose of endeavouring to obtain it. The distilled fluid carried over with it a small quantity of a colourless oil which rapidly became red, and in the course of a few days absolutely black, and proved to be a mixture of an oil insoluble in acids, and a series of bases of very remarkable properties obviously related to one another, and which I designate provisionally by the name of *pyrrol bases*.

When these substances had been entirely expelled, for which long-continued ebullition is requisite, slaked lime was added, and the bases which had been retained by the acid distilled over. A watery solution was obtained, from which the bases were separated as an oily layer by the addition of solid caustic potash. The potash solution still containing a considerable quantity of the more volatile bases, which could only be separated by the use of a very large quantity of potash, was distilled in glass vessels, and the product collected in a succession of three receivers, the first kept cold by water, the second by a freezing mixture, and the third containing hydrochloric acid for the purpose of condensing ammonia and another gaseous base by which it was accompanied. The first receiver contained the oily bases, which could now be separated by a comparatively small expenditure of potash; in the second only a few drops of fluid were found; while the hydrochloric acid in the third was saturated with ammonia and another gaseous base. This last solution was evaporated; the chloride of ammonium, which deposited in succession crops of crystals, was separated; and at length there was obtained a dark mother-liquor which, on cooling, solidified into a mass of foliated crystals deliquescent in moist air. These were dissolved in absolute alcohol for the separation of traces of sal-ammoniac, and purified by animal charcoal They were thus obtained in long, transparent and colourless plates, with a pungent and bitter taste. Treated with potash, they evolved a

gaseous base having an ammoniacal and putrid odour.   They gave a platinum-salt in fine golden-yellow scales, the analysis of which corresponded completely with the formula, $C_2 H_9 N . HCl. PtCl_2$; the base is consequently *methylamine*.

The oily bases were dried by means of caustic potash, and distilled in a retort with a thermometer.   Ebullition commenced at about 150° F.; at 212° the receiver was changed, and the oil distilling above that temperature collected in fractions of 10° each.   The portion boiling under 212° was rectified and collected in fractions of 5° each, which were nearly equal in bulk.   They were all very similar in properties, possessing a high refractive power, and a pungent odour very like that of ammonia in the lower fractions.   Exposed in the anhydrous state to a mixture of snow and salt, they remain perfectly fluid, but if a little water be added, crystals of a hydrate are deposited.   The quantity of those bases which I obtained was too small to admit of complete separation by fractionated distillation; I therefore converted portions of those fractions, which I had reason to believe corresponded to particular bases, into platinum salts.   I selected in the first instance the most volatile fraction, which boiled under 150°, and obtained from it a beautiful yellow salt, readily soluble in cold water, still more so in boiling water, and depositing in golden scales, which gave analytical results corresponding with the formula $C_6 H_9 N . HCl . PtCl_2$.   The base is therefore *propylamine*, which I have already obtained by the action of potash upon codeine. Having obtained these bases, ethylamine, the intermediate term of the same series, was next sought for; and by collecting the first few drops of the lowest fraction apart, a platinum-salt was obtained, which was obviously a mixture of those of ethylamine and propylamine, but of which the quantity was too small to admit of purification by re-crystallization.   The occurrence of these bases enables us to establish satisfactorily the constitution of petinine, which must obviously be $C_8 H_{11} N$ and not $C_8 H_{10} N$, as I formerly supposed it.   Indeed, the analysis of the platinum-salt contained in the first part of this paper, fully agrees with the latter formula, though that of the base itself differs from it; but much less reliance is to be placed upon that analysis, as it is difficult to obtain the base itself sufficiently pure. It thus appears that the products of destructive distillation contain ammonia and the first four members of the series of bases homologous with it; but it is probable that that series does not end here, as distinct indications of the presence of amylamine were found; and it is possible that caproamine may also be detected; but here the series ends, as when we reach a temperature of about 240°, the character of the bases alters, and we enter upon an entirely different series.

The separation of the bases, boiling above 240°, has been attended with great difficulties; but after a trial of many different processes, such as converting them into salts, exposure to cold, partial satura-

tion, &c., fractionated distillation was found the most advantageous, though even that was extremely troublesome, and I was by no means so successful in obtaining fixed boiling points, as I had been when operating on a smaller scale. All the oils, boiling above 212°, were submitted to a systematic course of fractionation, each fraction being distilled alone, and the product collected in a fresh series of receivers, which were changed at every 10°. After fourteen rectifications, the fractions, which had at first spread themselves at each successive distillation over a very large number of degrees, were confined to a comparatively small range, and it was obvious that a separation was being effected, although with extreme slowness. At this point, I endeavoured, by examination of the platinum salts obtained at different temperatures, to ascertain the constitution of the bases which those fractions contained, and knowing from previous experiments that that boiling between 270° and 280° consisted of picoline, I had indications of where these were likely to be found, and have thus been enabled to determine the existence of two bases homologous with that substance.

Pyridine.—The first of these bases, to which I give the name of pyridine, occurs in the fraction boiling about 240°. It is a perfectly transparent and colourless oil, which is not coloured by exposure to the air. Its odour is similar to that of picoline, but more powerful and pungent. It dissolves in water in all proportions, and is also readily soluble in the fixed and volatile oils. Acids dissolve it with the evolution of much heat, and the formation of highly soluble salts. With bichloride of platinum it gives a double salt in the form of flattened prisms, tolerably soluble in boiling water, less so in alcohol, and entirely insoluble in ether. When these crystals are boiled for a considerable time in water, they appear to undergo decomposition, with the formation of a platinum-salt crystallizing in golden yellow scales. The analysis of this salt gave results corresponding with the formula

$$C_{10} \, H_5 \, N \, . \, HCl \, . \, PtCl_2.$$
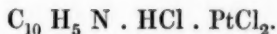
The formula of the base itself must consequently be $C_{10} \, H_5 \, N$., a member of the picoline series. I have not yet extended my investigation of this base further, as the phenomena observed in the examination of the next substance showed that much difficulty would still be experienced in its purification.

Lutidine.—In the fraction boiling about 310°, occurs a base which has exactly the constitution of toluidine. The fraction obtained at 305° to 310° in the distillation of the mixed bases gives more distinct indications of a fixed boiling point, than that obtained at any other temperature. It is much less soluble than those of lower boiling points, and when dropped into a small quantity of water, floats on the surface, and is only slowly dissolved on agitation. It is less soluble

in hot than in cold water, and separates as an oily layer when its cold saturated solution is gently heated.   Its odour is more aromatic than that of picoline.   It unites with the acids and forms highly soluble salts.   Its analysis gave results corresponding closely with the formula $C_{14} H_9 N$.   Notwithstanding the close correspondence of the analytical results, it appeared on further experiment that in some of the portions analyzed, appreciable quantities of picoline were present; for when a portion was converted into platinum-salt, the first crystals which deposited were found to contain 32·8 per cent of platinum, which is the number for the picoline salt; but on evaporating, further crystals were deposited, containing 32·5 and 32·0 per cent of platinum; and the mother-liquor of these, in addition of alcohol and ether, gave a salt in flattened tables, which analysis proved to be the pure lutidine salt.   This salt crystallizes in square tables, sometimes very regular, at other times confused and imperfect.   It is very soluble in cold, and still more so in hot water, and is also extremely soluble in excess of hydrochloric acid.   The analysis of the pure salt corresponded with the formula,

$$C_{14} H_9 N . HCl . PtCl_2.$$
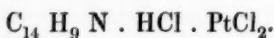
It is clear that this salt is that of the base of which the analysis has been given; but it is equally obvious that, notwithstanding the close approximation of the results to theory, the base had never been obtained absolutely pure, but had retained more or less picoline.   In the course of this investigation, I have been frequently struck with the fact that when the fraction corresponding to any particular base is analyzed, results closely approximating to theory are obtained, even when the substance is very far from being pure.   I found, for instance, that the portion boiling between 270° and 280°, after one or two rectifications, gave exactly the numbers for picoline, although when again rectified, it commenced boiling at about 250°, and a small quantity remained in the retort at 300°.   But it is readily intelligible that this should be the case where we have to deal with a series of homologous bases, in which the percentage of carbon increases as the boiling point rises, so that we have the excess of carbon in the less volatile, counterbalancing the deficiency in the more volatile, and as each rectification removes equal quantities of the more and the less volatile bases, the percentage composition of the intermediate substance must remain unchanged.

Hydrargochloride of Lutidine.—I directed my attention to this compound, in the hope that it might prove suited to the purification of the base, but soon abandoned it, as I found it impossible to obtain invariably the same compound.   When a solution of corrosive sublimate in alcohol is added to an alcoholic solution of lutidine, a curdy white precipitate falls immediately, unless the solutions be highly dilute, in which case it is deposited slowly in groups of radiated

needles. It dissolves in boiling water, with partial decomposition, and is still more soluble in spirit, from which it is deposited in crystals on cooling.   Its analysis corresponded with the formula $2HgCl + C_{14} H_9 N$. In another preparation, a salt was formed which corresponded nearly with the formula $3HgCl + C_{14} H_9 N$, and intermediate results were also obtained; but as the existence of these different compounds appeared fatal to their employment as a means of purifying the bases, I did not pursue their examination further.

It appears then that Dippel's oil contains two series of bases, one homologous with ammonia, the other peculiar to the oil, homologous with one another, and remarkable for their isomerism with the series of which aniline is the type.   Thus we have,

Pyridine . . . $C_{10} H_5 N$

Picoline . . . $C_{12} H_7 N$ . . . Aniline

Lutidine . . . $C_{14} H_9 N$ . . . Toluidine.

And it is probable that the series does not cease here, as I have found that the fractions of base with higher boiling points give a steadily decreasing percentage of platinum.   It is impossible in the present state of the investigation to give any opinion as to the intimate constitution and relations of these two series of what may be called isohomologous bases. The most obvious explanation would be to suppose the new bases to be imidogen or nitrile bases; but into those questions I shall not now enter, but reserve their consideration for a future paper.

Pyrrol bases.—I have already referred to another series of bases which I call provisionally *pyrrol bases*, which distil away from the acid by which the others are retained.   They are obtained in the form of an oil insoluble in water, and which, though at first colourless, soon becomes red, and finally black, and gives with hydrochloric acid and a piece of fir wood, the peculiar purple-red colour which Runge describes as characteristic of pyrrol.   I imagined at first that I had actually obtained this substance, which had escaped me in my previous experiments, but soon found I had to deal with a mixture of several bases; for when distilled with the thermometer, it began to boil about 212°, and gave a series of fractions up to above 370°. These oils were all bases, with a peculiar and disgusting odour, quite different from, and much more disagreeable than the picoline bases. They dissolve easily in a small quantity of hydrochloric acid, and give with bichloride of platinum a yellow precipitate, which is rapidly converted into a black substance.   When heated with an excess of acid, they present a very remarkable character; the solution at a certain temperature becomes filled with red flocks so abundant and bulky, that if not too dilute, it becomes perfectly solid, and the vessel may be inverted without anything escaping.   The same change takes place, though more slowly, in the cold.   When this substance is

collected on a filter, washed and dried, it forms a reddish-brown porous mass insoluble in water, acids, and alkalies, but soluble in alcohol.

The acid fluid separated from this substance by filtration, when supersaturated with an alkali, evolves the odour of the picoline bases, whence I infer that the pyrrol bases are in all probability coupled substances containing the picoline series in combination with some substance which yields the red matter.

I have not as yet paid much attention to the non-basic portion of bone-oil, but I have found that by repeated rectifications it improves in odour, and that benzine is contained in the more volatile portions. It is probable, therefore, that the series of homologous carbo-hydrogens to which benzine belongs, may constitute a part but not the whole of the oil, as I have found that when boiled with potash, ammonia is gradually evolved; and on saturating the potash solution with sulphuric acid, the odour of butyric acid, or at least one of the fatty acids, is evolved; whence I conclude that it also contains the nitriles of those acids.

On Rubian and its Products of Decomposition.

By Edward Schunck, F.R.S.

(ABSTRACTED BY THE AUTHOR.)

PART I.

Among the many discussions to which the subject of madder has given rise among chemists, there is none which is calculated to excite so much interest as that concerning the state in which the colouring matter originally exists in the root, and there is no part of this extensive subject which is at the same time involved in such obscurity. It is a well-known fact, that the madder-root is not well adapted for the purposes of dyeing until it has attained a growth of from eighteen months to three years, and that after being gathered and dried, it gradually improves for several years, after which it again deteriorates. During the time when left to itself, especially in a state of powder, it increases in weight and bulk (in consequence, probably, of absorption of moisture from the air), and some chemical change is effected, which, though not attended by any striking phenomena, is sufficiently well indicated by its results. There are few chemical investigations that have thrown any light on the nature of the process which takes place during this lapse of time, and, in fact, most of the attempts to do so have merely consisted of arguments based on analogy. It has been surmised that the process is one of oxidation, and that the access of atmospheric air is consequently necessary; but a more general supposition is, that the process is one of fermentation, attended perhaps by oxidation. What the substance is, however, on which this

process of oxidation or fermentation takes effect, and what the products are which are formed by it, are questions which have never been satisfactorily answered. It has indeed been suspected by several chemists, that there exists originally some substance in madder, which by the action of fermentation or oxidation, is decomposed, and gives rise by its decomposition to the various substances endowed either with a red or yellow colour, which have been discovered during the chemical investigations of this root; and to this view Persoz, in his " Traité de l'Impression des Tissus,"* gives his assent.

To Mr. J. Higgin† is due the merit of having first called attention to the fact, that important changes take place during the process of dyeing with madder, which can only be explained by supposing that an actual formation of colouring matter takes place during the process. Mr. Higgin concluded from his experiments that a formation of part of the colouring matter, during the dyeing process, is due to the peculiar substance, called by Kuhlmann, *Xanthine.*

A very simple experiment suffices to prove that madder, in its dry state, contains very little, if any alizarine ready formed. If an extract of madder be made with cold water, it will be found that the brownish-yellow liquid thus obtained, when gradually heated, will dye as well and as strongly as the madder from which it has been pressed. Now, if the colouring matter were originally present in the form of alizarine, this could not take place, since alizarine is almost insoluble in cold water; and in employing it for the purpose of dyeing, it is necessary to dissolve it in warm or boiling-water, before it begins to exert any effect, as is plainly seen in the case of garancine, which contains alizarine ready formed.

By adding a variety of substances to an extract of madder with cold water, I was enabled to ascertain under what circumstances, and by what means the tinctorial power of the liquid is destroyed, and consequently what is the general character of the substance or substances to which it is due. I found that by adding sulphuric or muriatic acid to the extract and heating, the liquid, after neutralisation of the acid, was no longer capable of dyeing. The tinctorial power was also destroyed by the addition of hydrate of alumina, magnesia, protoxide of tin, and various metallic oxides, but not by carbonate of lime or carbonate of lead. In all cases in which the property of dyeing in the extract was destroyed, I invariably found that its bitter taste and bright yellow colour were lost. In my former papers on this subject, I have shown that the intensely bitter taste of madder and its extracts is due to rubian; and hence it follows that this substance, though itself no colouring matter, is in some way concerned in the changes when by a formation of colouring matter is induced in aqueous extract of madder.

* T. I., 501.
† On the Colouring Matters of Madder, by J. Higgin, Phil. Trans. for Oct. 1848.

The preparation of rubian in a state of purity is attended with difficulties, in consequence of the facility with which it is decomposed by most reagents. There is also another circumstance which presents obstacles to almost all attempts to obtain it pure. There is no investigation of madder which does not make mention of a substance, which when its watery solution is mixed with sulphuric or muriatic acid, and boiled, gives rise to the formation of a dark green powder. To this substance, which possesses no bitter taste, and is in fact devoid of any characteristic property except the one mentioned, I have restricted the name *xanthine*. The xanthine of most other chemists is, however, a mixture of rubian with this substance, and possesses therefore the bitter taste of the former, while showing the characteristic behaviour of the latter towards acids. To avoid confusion, I shall no longer employ the name of xanthine, and I shall call the substance which gives the green powder, with acids, *chlorogenine*. Now these two substances, though of very different nature, behave similarly towards many reagents. Chlorogenine, for instance, is not precipitated by basic acetate of lead, when it is contained alone in solution ; but it is partly precipitated thereby, when rubian is present at the same time.

After numerous experiments I discovered a property of rubian, which is perhaps more characteristic of it than any other, and that is the remarkable attraction which is manifested by it towards all substances of a porous, or finely-divided nature; and it was this property by means of which I was enabled to obtain it in a state of purity. If to a watery extract of madder, a quantity of protochloride of tin be added, a light, purple-lake is precipitated. Most of the rubian remains in the solution, which still retains its yellow colour and bitter taste. If, however, after filtering, sulphuretted hydrogen be passed through it, then provided the quantity of tin, still in solution be sufficiently large, the sulphuret of tin at the moment of precipitation, carries down the whole of the rubian, and the solution loses its bitter taste, and the greater part of its yellow colour. The whole of the chlorogenine remains in solution, and may easily be detected in the filtered liquid by means of acids. If the sulphuret of tin, after being collected on a filter, and well washed with cold water until the percolating liquid no longer gives a green colour on being mixed with acid and boiled, be treated with boiling alcohol, a yellow solution is obtained, which, on evaporation, gives pure rubian, without any admixture of chlorogenine, in the shape of a dark yellow, brittle substance. The same effect is produced by sulphuret of lead. If sugar of lead be added to an extract of madder, a dark, reddish-brown precipitate falls, the liquid still containing the rubian of the extract, as seen by its deep yellow colour and bitter taste. If sulphuretted hydrogen be now passed through the filtered liquid, a great part of the rubian goes down with the sulphuret of lead, and may again be separated from it by means of boiling alcohol.

This attraction of surface exerted towards rubian by bodies in a state of minute division, is not confined to metallic sulphurets. A very small quantity of animal charcoal is sufficient to deprive an aqueous extract of madder of its bitter taste and its tinctorial power. Lamp-black acts in the same manner, though much less powerfully. Wood charcoal, however, has no absorbent effect whatever on rubian. All these substances attract rubian alone, leaving the other substances contained in the extract, such as chlorogenine, sugar, and pectine, untouched. By means of boiling alcohol, part of the rubian in combination with them is again removed, and thus an easy and efficient means is given of obtaining rubian in a state of purity.

The following method of operation I have found best adapted for the purpose. A weighed quantity of madder being placed on a piece of calico or fine canvas, stretched on a wooden frame, boiling water is poured on it, in the proportion of 4 quarts of water to 1 of madder. A dark yellowish-brown liquor is obtained, to which there is added, while hot, for every pound of madder taken 1 oz. of animal charcoal. The liquid being well stirred with the charcoal, the latter is allowed to settle, which it does in a very short time, and the liquid, which still retains a brown colour, is decanted. The charcoal is then placed on a piece of calico, or on a paper filter, and washed with cold water, until the percolating liquid, when mixed with muriatic acid and boiled, no longer acquires a green colour, which is a sign that the chlorogenine is removed. The animal charcoal is now treated with boiling alcohol, which is filtered boiling hot, and the treatment is repeated until it no longer communicates to the alcohol any yellow colour. The alcohol is now evaporated. During evaporation, a small quantity of a dark flocculent substance is deposited, which is separated by filtration. The solution still contains a small quantity of another substance, which is a product of decomposition of rubian itself, and is probably formed by the application of too great a heat in the process of drying the madder. This substance may be removed by adding sulphuric acid to the cold solution after the greatest part of the alcohol has been removed. The sulphuric acid completely decomposes the foreign substance, provided a sufficient quantity is employed, and converts it into a substance which renders the solution milky, and then falls in the shape of brown resin-like drops. The sulphuric acid being neutralized with carbonate of lead, the filtered solution, which is yellow, and now contains pure rubian, is carefully evaporated to dryness. From 1 cwt. of madder, I obtained in this manner about 1000 grs. of rubian.

As thus prepared, rubian has the following properties. It is a hard, dry, brittle, shining, perfectly uncrystalline substance, similar in appearance to gum or dried varnish. It is not deliquescent, as xanthine is described to be. In thin layers it is perfectly transparent,

and of a beautiful dark yellow colour.   In large masses it is dark brown.   It is very soluble in water and alcohol, more so in the former than the latter, but insoluble in ether.   Its solutions have an intensely bitter taste.   Its watery solution gives no precipitates with the mineral or organic acids, nor with salts of the alkali or alkaline earths.   The only metallic salt which precipitates it from its solution is basic acetate of lead.   The precipitate is light red.   Concentrated sulphuric acid dissolves rubian with a blood-red colour; on boiling the solution, it becomes black and disengages sulphurous acid. Dilute sulphuric and muriatic acids decompose it on boiling in a manner to be described below.   Nitric acid changes it into the acid which I called in my former papers alizaric acid, and which Laurent and Gerhardt consider as identical with naphthalic acid.   Phosphoric, oxalic, tartaric, and acetic acids, produce no effect on rubian. When a stream of chlorine gas is passed through a watery solution of rubian, the solution immediately becomes milky, and begins to deposit a lemon-yellow powder, into which, on continuing the action, the whole of the rubian is converted, the liquid becoming colourless. Caustic soda turns the colour of a solution of rubian from yellow to blood-red, which on boiling the liquid again changes to purple. When heated on platinum-foil, rubian melts, swells up very much, burns with a flame, and leaves a carbonaceous residue.   When heated gradually in a tube, it begins to undergo decomposition, accompanied by loss of water, at a temperature of about 130° C. When heated still further, it gives fumes of an orange colour, which condense on the colder parts of the vessel to a crystalline mass, consisting chiefly of alizarine.

The composition of rubian is expressed by the formula $C_{56}H_{34}O_{30}$, that of its lead-compound by $C_{56}H_{34}O_{30} + 6\,PbO$.

Action of sulphuric and muriatic acid on rubian.—The action of these two acids is precisely the same; but for the purpose of studying it, it is better to employ sulphuric acid, as it is more easily removed again afterwards.   On adding sulphuric acid in considerable quantity to a watery solution of rubian, and boiling the liquid, no perceptible change takes place at first, except that the solution loses a little of its transparency, and becomes slightly opalescent.   After boiling for some time, the rubian is entirely decomposed.   On allowing to cool, a quantity of orange-coloured flocks are deposited, while the liquid becomes almost colourless.   The orange-coloured flocks are separated by filtration, and washed with cold water, until all the acid is removed.   They now consist of four different substances, viz.: firstly, *Alizarine;* secondly, the substance which in my former papers I have called *alpha-resin,* but to which I prefer giving the name of *Rubiretine;* thirdly, the substance which I formerly termed *beta-resin,* but which I shall now call *Verantine,* from *Verantia,* the name applied to madder in the middle ages.   The fourth substance has

not hitherto been observed. I shall call it *Rubianine*. On dissolving the mixture of these four substances in a small quantity of boiling alcohol, the rubianine separates, on the solution cooling, as a brownish-yellow crystalline mass, and is purified by recrystallization from boiling alcohol. On adding acetate of alumina to the alcoholic liquid, a dark red precipitate falls, which consists of alizarine and verantine in combination with alumina. The compound is decomposed with acid; the mixture of alizarine and verantine is again dissolved in alcohol; and the verantine is precipitated by means of acetate of copper, a compound of alizarine and oxide of copper remaining dissolved in the alcohol, and forming a dark purple solution. The rubiretine is contained in the liquid from which the alizarine and verantine have been precipitated by acetate of alumina. The acid liquid from which the orange-coloured flocks were deposited, contains a species of *sugar*, which is obtained by neutralising the acid with carbonate of lead, and evaporating.

The analysis of the alizarine formed in this process led to the same formula, at which I had previously arrived, viz., $C_{14}H_5O_4$, and this formula receives a new confirmation from the relation in which it stands to that of rubian. The formation of alizarine from rubian admits of a very easy explanation. By simply losing 14 equivs. of water, 1 equiv. of rubian is converted into 4 equivs. of alizarine; for:

$$C_{56}H_{34}O_{30} = 4\,C_{14}H_5O_4 + 14\,HO.$$
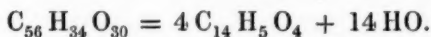
The properties of verantine are identical with those of the substance to which I formerly gave the name of the beta-resin of madder. Its composition is expressed by the formula $C_{14}H_5O_5$, which was confirmed by the analysis of the baryta and copper compounds.

The most probable formula for rubiretine is $C_{14}H_6O_4$. If, therefore, 2 equivs. of verantine, 2 equivs. of rubiretine, and 12 equivs. of water, be added together, the sum will be equal to 1 equiv. of rubian; for,

$$2\,C_{14}H_5O_5 + 2\,C_{14}H_6O_4 + 12\,HO = C_{56}H_{34}O_{30}$$
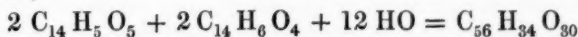
Rubianine is soluble in boiling alcohol and water, from which it crystallizes, on the solutions cooling, in bright, lemon-yellow, silky needles, which, when dry, form an interwoven mass. When heated it is carbonised without being volatilised. It is not decomposed by boiling nitric acid. It dissolves in solutions of alkalies with a blood-red colour, but after some time is again deposited unchanged. Its alcoholic solution gives no precipitate with sugar of lead. It is not converted into rubiacic acid by means of persalts of iron, by which it is chiefly distinguished from rubiacine. Its composition is expressed by the formula $C_{32}H_{19}O_{15}$.

The sugar mentioned above as the fifth product of the action of

acids on rubian is obtained in the form of a yellow transparent syrup, which neither crystallises, however long its solution may be left to stand, nor becomes dry, unless heated to 100° C. Its taste is sweetish, accompanied by a bitter after-taste, like that of burnt sugar. It is easily decomposed by caustic alkalies; but not so easily by dilute sulphuric acid. Nitric acid converts it into oxalic acid. By fermentation it yields alcohol. Its composition is identical with that of grape-sugar, its formula being $C_{12}H_{12}O_{12}$. Hence, it follows, that 1 equiv. of rubian takes up 9 equivs. of water, and then splits up into 1 equiv. of rubianine, and 2 equivs. of sugar, for

$$C_{32}H_{19}O_{15} + 2\,C_{12}H_{12}O_{12} = C_{56}H_{34}O_{30} + 9\,HO.$$
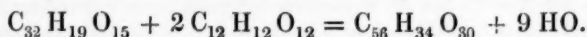
In the opinion of most chemists who have examined madder, this root contains two distinct colouring matters, viz., alizarine, and another, to which the names of *purpurine, oxylizaric acid*, and *madder-purple*, have been applied by different chemists. I have, however, reason to suppose that the latter is in fact no distinct colouring matter, but a mixture of alizarine and verantine. As a characteristic of purpurine, is mentioned its property of forming, when treated with boiling alum-liquor, a red, opalescent solution, from which it separates again in orange-coloured flocks on the solution cooling. Pure alizarine is not more soluble in boiling alum-liquor than in water; it only communicates to the liquor a yellow colour. Verantine is still less soluble in alum-liquor. If, however, a mixture of alizarine and verantine be dissolved in caustic alkali, and they be then precipitated together by means of a solution of alum added in excess, then, on boiling the precipitate with the liquid, a bright red solution is obtained, and on filtering and allowing to cool, orange-coloured flocks are deposited, while the liquid still remains red, but gives a yellow precipitate on the addition of acid. From this experiment, I am inclined to infer that alizarine and verantine are capable of forming a double compound with alumina, soluble in boiling water, and that a mixture of the two in the proportion in which they exist in this compound, constitutes what has been called purpurine.

On Aspartic and Malic Acids.

By L. Pasteur.[*]

In a former memoir, the author has shown that aspartic and malic acids have the power of turning the plane of polarization of luminous rays, and that this power likewise extends to all their saline compounds; moreover, that fumaric acid, as formed in nature, and likewise

as it is obtained by the dry distillation of malic acid, does not possess this property. About the same time, M. Dessaignes announced the transformation of acid fumarate of ammonia into malic acid. On comparing the results obtained by Dessaignes with those of Pasteur, it would appear that aspartic acid, a substance possessing rotatory power, may be obtained artificially from acid fumarate of ammonia, a substance which is destitute of that property. Now, as such a result would be contrary to all previous experience, the author was disposed to conclude that the aspartic acid formed by Dessaignes differed from natural aspartic acid—that, namely, which is formed from asparagine—by the absence of molecular rotatory power. Accordingly, he obtained from M. Dessaignes a specimen of the aspartic acid prepared from fumarate of ammonia, and on examining it, found that it was really destitute of rotatory power, although in its chemical properties, it exhibited the most exact resemblance to natural aspartic acid.

It became therefore peculiarly interesting to examine the transformation of this substance into malic acid. It is well known that malic acid may be readily formed from asparagine and aspartic acid; and the author has shown that the acid thus obtained is identical, in its chemical, crystallographical, and optical properties, with the malic acid of the service-tree, the apple, and the grape. Now, on treating the new aspartic acid of Dessaignes by a method exactly similar to that by which Piria obtained malic acid from asparagine, a malic acid was produced which was likewise destitute of rotatory power. The author proposes to distinguish these acids and their derivatives by the names actually in use, with the addition of the epithets *active* and *passive*; e. g., *active malic acid, active aspartic acid, inactive malic acid, inactive aspartic acid.*

A comparison of the properties of these active and passive compounds presents very curious and unexpected results. With the exception of a few dissimilarities, for the most part of minor importance, these substances are, chemically speaking, undistinguishable. Every reaction which can be produced by one of the active acids, may likewise be obtained, under similar circumstances, with the corresponding passive acid; and the resulting compounds have always the same ultimate composition and the same chemical properties. Thus, active malic acid, when heated to nearly 150° C., is transformed into two volatile acids, the *maleic* and *fumaric*. The same phenomenon is presented by inactive malic acid. Active malate of lead fuses at a temperature below 100°; so likewise does the inactive malate. Active malate of lead, which is amorphous when first precipitated, subsequently crystallizes in silky tufts; inactive malate of lead exhibits the same property. All the active malates and aspartates, without exception, have their analogues among the inactive malates, which latter are obtained by exactly the same processes as the active

salts.   Lastly, the corresponding salts have always the same chemical formula.

The crystalline forms of the corresponding active and inactive compounds present some remarkable peculiarities, being sometimes totally distinct and incompatible, sometimes sensibly the same and with the same angles.   Thus, active aspartic acid and aspartate of soda crystallize in the system of the right prism with a rhombic base, whereas the corresponding inactive compounds crystallize in the system of the oblique prism with rectangular base, which is incompatible with the preceding.   On the other hand, the active bimalates of lime and ammonia crystallize in the system of the right prism with rhombic base, and the corresponding inactive bimalates, not only crystallize in the same system, but likewise with the same angles; there is this difference, however, that the active substances always exhibit hemihedral faces, which the inactive compounds never do.   It appears then, that the molecular constitution of the inactive substances is not incompatible with a crystalline form identical with that of the corresponding active compounds; and we may presume with tolerable certainty that where the forms appear incompatible, the incompatibility is due to dimorphism.

The phenomena above described might induce the supposition that the inactive varieties of aspartic and malic acid might each be separated into two other acids, one of which would turn the plane of polarization to the right, and the other to the left, in the same manner as racemic acid is separated into dextroracemic and lævoracemic acid.   This supposition, however, is untenable.   For, in the first place, the difference between racemic and tartaric acid is much greater than that which exists between active and inactive malic acid.   Thus, the chemical composition of a racemate is rarely identical with that of the corresponding tartrate; and, in the few cases in which this identity of composition exists, the racemate is separable by crystallization into a dextro- and a lævo-tartrate.   But the chief objection to the above-mentioned supposition is derived from the mode of production of inactive aspartic and malic acids.   Inactive aspartic acid is in fact derived from maleic and fumaric acids.   If then it possesses a binary constitution, an analogous constitution must be supposed to exist in the acids from which it is derived—unless indeed we suppose that the maleic and fumaric acids are transformed by·heat into binary *symmetrical* groups—a change which there is even greater difficulty in conceiving.   Now, to suppose a binary constitution in fumaric and maleic acids, is to admit that the action of heat transforms a molecule of active malic acid into binary groups of two active molecules identical in form, but not superposible.   On the other hand, it is reasonable to suppose that a molecular arrangement unsymmetrically constituted, may, when exposed to an elevated temperature, be changed into another molecular arrangement, in

which the peculiar disposition which produced the want of symmetry in the first arrangement, has disappeared.*

The results above described throw a new light on the molecular constitution of bodies. The author had shown in former researches, that substances capable of acting on polarized light, may be compared to those groups, so frequent in the vegetable and animal kingdoms, in which the want of symmetry is of that nature that we may imagine other groups identical with them in form, but not superposible; *e. g.*, the right and left members of the body, and those plants in which the points of insertion of the leaves form a right-hand or a left-hand spiral. In one case (that of tartaric acid) the left-hand modification corresponding to the right-hand variety previously known, was actually discovered. In the present instance, we see that compounds exerting a rotatory power on polarized light may be so little altered in their molecular grouping, as to retain without exception all their chemical properties, and merely to lose that peculiar unsymmetrical molecular grouping, which produces the right or left-handed character.

The only known substances which can be compared with those just considered are ordinary active oil of turpentine, and the inactive variety obtained by the action of heat and caustic lime on the artificial solid camphor of turpentine. It is highly probable, however, that this new kind of isomerism is a general property of substances possessing the rotatory power, and that examples of the same kind will be multiplied, now that the attention of chemists has been drawn to this new class of compounds.

A remarkable similarity appears to exist between the molecular constitution of ordinary malic acid and that of tartaric acid. Biot, it is well known, has discovered several remarkable peculiarities in the action of tartaric acid upon light, viz.: 1. That its rotatory power increases with the proportion of water which it contains; 2. That this power is increased by elevation of temperature; 3. By the presence of boracic acid; 4. That the mode of dispersion of the planes of polarization does not follow the law of the inverse squares of the lengths of the wave, which is found to be very nearly true in quartz and in most substances possessed of molecular rotatory power. These four exceptional laws have hitherto been considered quite peculiar to

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* Bimalate of ammonia becomes inactive by the abstraction of 5 atoms of water at 200° C., and aspartic acid by the loss of 3 atoms. The loss of rotatory power may be attributed to several causes: 1. The action of heat. 2. The expulsion of water, the molecular group before the loss of water, being unsymmetrical, in consequence of the disposition of the atoms of water in the midst of it. 3. We may suppose that the rotatory power was due to the relative arrangement of the molecules of water and of the de-hydrated substance. It would be very useful towards the solution of this important question, to abstract the molecules of water from the active groups at low temperatures, and ascertain whether the rotatory power is destroyed under those circumstances.

tartaric acid.   Pasteur, however, finds that active malic acid exhibits
the same peculiarities.   There must therefore be some intimate rela-
tion between the molecular constitution of tartaric and of malic acid;
and it must be especially remarked that this analogy of constitution
is shown by a dissymmetric phenomenon, viz., the optical rotatory
power.   Hence it follows, independently of any theoretical generaliza-
tions of the facts relating to right and left-handed substances—that
since there are two varieties of tartaric acid, the one right and the
other left-handed, there must likewise exist two corresponding varie-
ties of malic acid.   It matters little whether the variety of malic acid,
which is *symmetrical* to the ordinary malic acid known to chemists,
exists or not in any particular plant.   That which we may safely
assert, is the possible existence of this variety of malic acid, *sym-
metrical* or *non-superposible* to the acid of the service-tree, of the
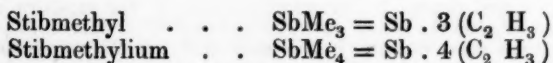apple, and the grape.

The ordinary active variety of malic acid corresponds to *dextro-
tartaric acid,* a fact which might have been predicted from the con-
stant simultaneous existence of malic acid and dextro-tartaric acid in
all acid fruits.   It is very probable that when the kind of grape which
yielded tartaric acid containing racemic acid shall have been redisco-
vered, this same grape will be found to contain the *lævo-malic* acid,
symmetrical to ordinary malic acid.

Another consequence which may be deduced from the preceding
facts, is the possible existence of an inactive asparagine corresponding
to the inactive malic and aspartic acids ; and when we shall have dis-
covered the mode of preparing ordinary active asparagine from active
malic or aspartic acid, the same reaction applied to the corresponding
inactive acids will doubtless produce inactive asparagine.

There are also strong reasons for presuming the existence of an
inactive tartaric acid corresponding to inactive malic acid.   This acid
would be neutral to polarized light, like racemic acid, but would differ
from the latter in molecular constitution, and would not be separable
into two symmetric acids.

Organic Bases containing Antimony.[*]

The compounds of this class discovered up to the present time are
as follows :

$$\text{Stibmethyl} \quad . \quad . \quad . \quad \text{SbMe}_3 = \text{Sb} . 3 \, (\text{C}_2 \, \text{H}_3)$$
$$\text{Stibmethylium} \quad . \quad . \quad \text{SbMe}_4 = \text{Sb} . 4 \, (\text{C}_2 \, \text{H}_3)$$

* Löwig and Schweitzer, Ann. Ch. Pharm. LXXV, 315, 327; J. pr. Chem.
XLIX, 385; L, 321; Pogg. Ann. LXXX, 338; Chem. Gaz. 1850, 201, 372, 395, 420.
—Landolt, Ann. Ch. Pharm. LXXVIII, 91; Löwig, *Grundriss der Organischen
Chemie*, Braunschweig, 1852, S. 383.

$$\text{Stibethyl} \quad . \quad . \quad . \quad . \quad \text{SbAe}_3 = \text{Sb} . 3 \, (\text{C}_4 \, \text{H}_5)$$
$$\text{Stibethylium} \quad . \quad . \quad . \quad \text{SbAe}_4 = \text{Sb} . 4 \, (\text{C}_4 \, \text{H}_5)$$
$$\text{Stibamyl} \quad . \quad . \quad . \quad . \quad \text{SbAm}_3 = \text{Sb} . 3 \, (\text{C}_{10} \, \text{H}_{11})$$

The compounds SbMe_3, SbAe_3, and SbAm_3 are obtained by distilling the iodide of methyl, ethyl, or amyl, with antimonide of potassium. They all oxidize very rapidly; and therefore in preparing them, the same precautions must be taken as in the preparation of cacodyl, viz., to exclude the air completely, and conduct the whole operation in an atmosphere of carbonic acid.

These compounds have remarkably strong combining tendencies, and unite at ordinary temperatures with oxygen, sulphur, selenium and the halogens, the act of combination being attended with considerable evolution of heat, sufficient in the case of stibmethyl and stibethyl, to produce inflammation.

The compounds formed with the elements just named, resemble in all their relations, the corresponding potassium-compounds, and may be transformed one into the other, by mutual decomposition. The so-called basic radicals, however, containing 3 eq. of methyl, &c., combine with 2 eq. of oxygen, sulphur, chlorine, &c., a character by which they also differ from cacodyl. The compounds containing 4 eq. of methyl or ethyl are precisely analogous to ammonium, combining only with 1 eq. of oxygen, sulphur, chlorine, &c. These last-mentioned compounds are formed by the action of iodide or bromide of methyl or ethyl on stibmethyl or stibethyl, in which case the haloid-compounds $\text{SbMe}_4 \, \text{I}$, $\text{SbAe}_4 \, \text{I}$, &c., are produced.

Stibmethyl, SbMe_3.—This compound is a colourless, heavy liquid, which has peculiar odour, is insoluble in water, but dissolves sparingly in alcohol, and readily in ether. When exposed to the air, it gives off thick white vapours, takes fire, and burns with a blue flame, with separation of metallic antimony.

Stibmethylium, SbMe_4.—Not yet obtained in the separate state.

Oxide of Stibmethylium, $(\text{SbMe}_4) \, \text{O} + \text{HO}$.—This compound is obtained by agitating an aqueous solution of iodide of stibmethylium $(\text{SbMe}_4) \, \text{I}$, with recently precipitated oxide of silver, filtering from the iodide of silver, and evaporating the filtrate *in vacuo* over sulphuric acid. White crystalline mass, having a highly caustic, alkaline taste, and analogous in all its relations to caustic potash. Dissolves readily in water and alcohol, but very sparingly in ether. Volatilizes unchanged at a high temperature. Heated with potassium, it gives off a spontaneously inflammable gas. This base saturates acids completely, forming salts precisely corresponding to the salts of potash; it likewise expels ammonia, and even baryta and lime, as well as all the heavy metallic oxides, from their combinations. The

precipitate which it forms in solutions of zinc and alumina, dissolves in excess of the precipitant. From copper-salts it throws down hydrated oxide of copper, insoluble in excess of the base, and does not dissolve a trace of oxide of silver. All its salts have a bitter taste.

Sulphate of Stibmethylium.—α. Neutral. $(SbMe_4) O . SO_3$ or $SbMe_4 . SO_4$.—Obtained by adding sulphate of silver to an alcoholic solution of the iodine-compound, filtering from the iodide of silver, and treating the filtered liquid with a mixture of alcohol and ether; or by adding the oxide of stibmethylium to a concentrated solution of the acid salt, till the acid reaction disappears, and then mixing the aqueous solution with alcohol containing ether. It first separates in oily drops, which however soon solidify, and form rhombic prisms.

β. Acid sulphate, $(SbMe_4) O . HO . 2 SO_3$ or $SbMe_4 SO_4 + HSO_4$. —Obtained by evaporating a solution of the neutral salt over the water-bath. Crystallizes in very beautiful square tables with truncated summits; they are very hard, dissolve readily in water, and with tolerable facility in alcohol; their taste is first sharp, and afterwards bitter.

Nitrate of Stibmethylium.—Formed by treating a solution of the iodide with nitrate of silver. It is soluble in water; has a rough and bitter taste; crystallizes in small needles; and detonates when heated.

Bicarbonate of Stibmethylium, $(SbMe_4) O . HO . 2 CO_2$ or $SbMe_4 . CO_3 + HCO_3$.—Formed by completely saturating the pure base with carbonic acid. Crystallizes in small needles arranged in stellate groups. Dissolves easily in water, has a slightly alkaline and bitter taste, and gives no precipitate with neutral magnesia-salts.

Iodide of Stibmethylium, $SbMe_4 I$.—Formed, as above-mentioned, by bringing stibmethyl in contact with iodide of methyl. Crystallizes in very beautiful six-sided tables, easily soluble in water and alcohol, sparingly in ether. Its taste is first saline, afterwards bitter. When heated in a test-tube, it gives off vapours which take fire spontaneously in the air, antimonious acid being separated at the same time. Acids separate iodine from this compound; the iodine may also be precipitated by silver-salts.

Iodide of Stibmethylethylium, $SbMe_3 Ae . I$.—Obtained by mixing stibmethyl with iodide of ethyl; it closely resembles the preceding compound.

Chloride of Stibmethylium, $SbMe_4 Cl$.—Obtained by evaporating the iodine with strong hydrochloric acid, and evaporating, or by decomposing the iodide with corrosive sublimate; but the best mode of obtaining it, is to saturate a solution of pure oxide of stibmethylium with hydrochloric acid, and evaporate. This compound forms

white crystals, which are easily soluble in water, less soluble in alcohol, and quite insoluble in ether ; they have a bitter taste, and, in other respects are precisely analogous to the iodine-compound.

Stibethyl, $SbAe_3 = 4$ vol. gas.—This compound forms a transparent, colourless, extremely mobile liquid, having a strong refracting power, and a disagreeable alliaceous odour, which, however, is very transient.   It is insoluble in water, but dissolves readily in alcohol and ether.   Does not solidify at $-29°$ C., boils at $158\cdot5°$.   Spec. grav. $= 1\cdot3244$.   Vapour-density $= 7\cdot44$.

Oxide of Stibethyl, $(SbAe_3)\,\ddot{O}_2 + 2\,HO$.—When stibethyl is introduced in a fine jet into oxygen gas, it immediately takes fire, and burns with a dazzling white light ; the same effect is produced in the air, excepting that the ignition does not take place till after several seconds, and is preceded by the formation of a thick, white fume.   If, however, the oxidation proceeds slowly, a transparent, syrupy mass is obtained, consisting of $(SbAe_3)\,O_2 + 2\,SbO_3$* (the so-called *ethylo-stybelic acid*).   The oxide is obtained in a state of purity by precipitating the sulphate with baryta-water, and separating the baryta which still remains in the filtrate by carbonic acid.   On evaporating the liquid, the oxide remains in the form of a viscid, transparent, and perfectly colourless mass, presenting no traces of crystallization.   It dissolves readily in water and alcohol, sparingly in ether ; has a bitter taste, is not poisonous, and does not excite vomiting.   It is not volatile.   Oxide of stibethyl behaves like an inorganic base, and forms with acids, a number of crystallizable salts which are very soluble in water.

Sulphate of Stibethyl, $(SbAe_3)\,O_2 \,.\, 2\,SO_3$, is obtained by decomposing sulphide of stibethyl with sulphate of copper.   Crystallizes in small, white prisms, which are inodorous, have an acid reaction, a bitter taste, and are soluble in water and alcohol.

Nitrate of Stibethyl, $(SbAe_3)\,O_2 \,.\, 2\,NO_5$.—Stibethyl takes fire with explosion when brought in contact with fuming nitric acid.   In dilute nitric acid, it dissolves like a metal, with evolution of nitric oxide gas.   This salt crystallizes from its aqueous solution, by spontaneous evaporation, in large, transparent, rhomboidal crystals, which dissolve easily in water and alcohol, have an acid reaction, a bitter taste, and fuse at $62\cdot5°$.   It deflagrates when heated.

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* This is the formula given in Löwig's recently published *Grundriss der Org. Chem.*   But in the original paper by Löwig and Schweitzer (Ann. Ch. Pharm. LXXV), it is stated that the slow oxidation of stibethyl yields two products, viz., a syrupy mass consisting of oxide of stibethyl $(SbAe_3)\,O_2$, and a white powder insoluble in ether, consisting of $(SbAe)\,O_5$.   This latter compound is called *Aethylstibylsäure*, the radical SbAe being called *Aethylstibyl.*

Sulphide of Stibethyl, $(SbAe_3) S_2$.—When an ethereal solution of stibethyl is boiled with washed flowers of sulphur, and the warm ethereal solution decanted from the excess of sulphur, the whole liquid solidifies in a few minutes, forming a mass of dazzling white crystals, which smell like mercaptan, dissolve easily in water and alcohol, and when heated above 100°, fuse into a colourless liquid. The introduction of a piece of potassium into the fused sulphide of stibethyl, causes an immediate evolution of vapours of stibethyl. The solution of sulphide of stibethyl precipitates all metallic salts as sulphides; dilute acids immediately decompose it, with evolution of sulphuretted hydrogen. Sulphide of stibethyl is not volatile. With SbS_3 it forms a yellow, insoluble compound, which smells like mercaptan, and contains $(SbAe_3) S_2 + 2 SbS_3$.

Selenide of Stibethyl.—Similar in composition and properties to the sulphide; it suffers decomposition, however, when exposed to the air, selenium being separated.

Iodide of Stibethyl, $(SbAe_3) I_2$.—Formed by adding iodine in small quantities to an alcoholic solution of stibethyl, as long as its colour disappears, and then diluting the alcoholic solution. Crystallizes in long, perfectly colourless needles; has a faint odour, a bitter taste, and is easily soluble in water, alcohol, and ether; fuses at 70°, and may be sublimed by careful heating. With chlorine, bromine, acids, and metallic salts, it behaves exactly like iodide of potassium; nitrate of silver immediately forms with it a precipitate of iodide of silver.

Bromide of Stibethyl, $(SbAe_3) Br_2$.—When bromine is added drop by drop to stibethyl, each drop produces combustion. But by adding bromine in very small quantities, as long as its colour disappears, to an alcoholic solution of stibethyl, which must be kept cold, and then mixing the solution with a large quantity of water, bromide of stibethyl separates in the form of a perfectly colourless, transparent liquid, which at —10°, solidifies in a snow-white, crystalline mass. It has an unpleasant odour, like that of turpentine, excites a copious flow of tears when heated; is insoluble in water, but dissolves readily in alcohol and ether; it is not volatile. In its chemical relations, it is precisely analogous to bromide of potassium.

Chloride of Stibethyl, $(SbAe_3) Cl_2$.—When stibethyl is dropped from a narrow tube into a flask filled with chlorine, it takes fire at the instant of contact. Hydrochloric acid gas is decomposed by stibethyl, with evolution of hydrogen and formation of chloride of stibethyl; the same action takes place when strong hydrochloric acid is poured upon stibethyl. On mixing a solution of nitrate of stibethyl with strong hydrochloric acid, chloride of stibethyl immediately separates in the form of a colourless, strongly refracting liquid. It smells like turpentine, tastes bitter, is insoluble in water, but dissolves readily in alcohol and ether; does not liquefy at —12°. Sp. gr. = 1·540.

It is not volatile.   In its chemical relations, it resembles chloride of potassium.

Stibethylium, $SbAe_4$.—Known as yet only in the form of iodide, which is obtained by adding iodide of ethyl to stibethyl.   The iodide crystallizes in long beautiful needles, which are easily soluble in water and alcohol.

Stibamyl, $SbAm_3$.—Clear, colourless liquid, which fumes in the air, but without taking fire.   It forms compounds analogous to those of stibethyl, but they are all liquid and insoluble in water.

Bismethyl or *Bismuthide* of *Ethyl :*[*] $BiAe_3$.   Bismethyl is obtained in the same manner as stibethyl, bismuthide of potassium being substituted for the antimonide.   Forms a slightly yellow, very mobile liquid, of sp. gr. 1·80, which can only be distilled with water.   Has a disagreeable odour, like that of stibethyl, and produces, even if only traces of it are inhaled, an extremely unpleasant, burning sensation on the tongue.   When exposed to the air, it emits dense vapours, and takes fire, diffusing a thick yellow smoke of oxide of bismuth.   With oxygen, the halogens, and sulphur, it combines in the same proportions as stibethyl; but the resulting compounds are less permanent; for instance, when an alcoholic solution of iodide of bismethyl is left to stand for awhile, pure iodide of bismethyl separates out.   Bismethyl when heated alone, is decomposed, with separation of bismuth and evolution of gaseous products. If suddenly exposed to a high temperature, it explodes with great violence.

Observations on Telluric Ethyl, or Telluride of Ethyl.

By W. Mallet.[†]

Wöhler, in his notice upon telluride of ethyl,[‡] states that it is dissolved by nitric acid with evolution of nitric oxide, and that on adding hydrochloric acid to this solution, a heavy colourless liquid is precipitated in oily drops.   The nature of this liquid was not further investigated.

Mallet, in pursuing this subject, has found that telluride of ethyl

* Löwig.   Grundriss der Organischen Chemie. S. 386.
† Ann. Ch. Pharm. LXXIX, 223.
‡ Ibid. XXXV, 112.

behaves like an organic radical. The substance was prepared by
Wöhler's process, viz., by distilling a concentrated solution of
sulphovinate of baryta with telluride of potassium. Its vapour has
an intense yellow colour.

In attempting to prepare a *telluric mercaptan*, $C_4 H_6 Te_2$, by dis-
solving in water a mixture of sulphovinate of baryta and telluride of
potassium in a flask previously filled with hydrogen gas, then satu-
rating the solution with telluretted hydrogen, and distilling, the only
product at first obtained was monotelluride of ethyl, $C_4 H_5 Te$. But
on continuing the distillation at a stronger heat, another liquid passed
over with the water, distinguished from the former by much greater
density, higher boiling-point, and an intense red colour, so that even
in small masses, it appeared black and opaque, like bromine; it had
an offensive odour. Analysis showed it consisted of *bitelluride* of
ethyl, $C_4 H_5 Te_2$.

Nitrate of Telluric Ethyl.—$C_4 H_5 TeO . NO^5$.—When a solution
of monotelluride of ethyl in nitric acid is evaporated to dryness at a
gentle heat, there remains a white, crystalline mass, which dissolves
perfectly in water, and burns away like gunpowder when heated.
Alkalies produce no precipitate in solutions of this salt, because
the base $C_4 H_5 TeO$, is soluble in water. Sulphurous acid, on the
contrary, immediately reduces the radical, which separates in dark-
red drops. Sulphuretted hydrogen produces an orange-coloured pre-
cipitate, which, on heating the liquid, fuses into heavy black drops,
doubtless consisting of the sulphur-compound of telluride of ethyl =
$C_4 H_5 TeS$.

Chloride of Telluric Ethyl, $C_4 H_5 TeCl$, separates in the form of
a colourless oil, on the addition of hydrochloric acid to a solution of
telluride of ethyl in nitric acid. At first, the liquid becomes milk-
white, but the compound soon collects in large, transparent drops,
which sink in the water. It has an offensive odour. It may be
distilled without decomposition, but its boiling-point appears to be
very high, for when distilled with water, it passes over very slowly.
By analysis, it was found to contain 50·55 per cent of tellurium, and
27·07 of chlorine, the calculated numbers being 49·81 Te and
27·63 Cl.

Oxide of Telluric Ethyl, $C_4 H_5 TeO$, is formed by treating the
chloride immersed in water with recently precipitated oxide of silver.
The liquid becomes warm, and chloride of silver is formed. The
filtered liquid is a solution of the oxide of telluric ethyl in water; and
on evaporation at a gentle heat, the oxide remains in the form of a
colourless, highly crystalline mass. The aqueous solution exhibits an
alkaline reaction with turmeric. The oxide, when heated in a tube, is
decomposed, with separation of metallic tellurium, and formation of an
oil having an offensive odour. When heated in the air, it burns with
a blue flame like tellurium. Sulphurous acid decomposes the solution,

and separates the telluride of ethyl in red drops.   Hydrochloric acid throws down the chloride in colourless drops.
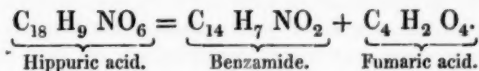
The oxide is likewise formed by direct oxidation of an alcoholic solution of telluric ethyl in the air; the process is, however, too slow to be practically available.   It is likewise obtained in the form of a sulphate, by treating telluride of ethyl with peroxide of lead and dilute sulphuric acid.

The solution of the oxide gives a yellow precipitate with chloride of platinum, and white with corrosive sublimate.   When it is mixed with chloride of ammonium—the solutions not being too dilute— ammonia is set free, and after a short time, a salt separates in small crystals arranged in stellate groups, and having exactly the form and the angles of gypsum.   This salt dissolves readily in hot water, and crystallizes out again unaltered on cooling.   By analysis, it was found to contain 26·73 per cent of tellurium and 15·45 of chlorine, numbers which appear to agree only with the formula $C_4 H_5 TeCl + 2 NH^4 Cl$, and with the supposition, that in the decomposition with the silver-salt, only one-third of the chlorine is separated.   But whether this is really the case, and what other compound is thereby formed, the author was unable to decide for want of material.

Examination of certain products obtained from Hippuric Acid.
By N. Socoloff and A. Strecker.[*]

There are few organic acids whose rational constitution has given rise to so many different opinions as that of hippuric acid.   From the decomposition which this acid undergoes by the action of per-oxide of lead, whereby it is converted into benzamide and carbonic acid, Fehling regarded it as a compound of benzamide with an acid (fumaric acid) convertible into carbonic acid by addition of oxygen: thus

$$\underbrace{C_{18} H_9 NO_6}_{\text{Hippuric acid.}} = \underbrace{C_{14} H_7 NO_2}_{\text{Benzamide.}} + \underbrace{C_4 H_2 O_4}_{\text{Fumaric acid.}}.$$

This view of the decomposition, however, is not quite satisfactory, inasmuch as fumaric acid is not altered by boiling with water and peroxide of lead.

Pelouze regarded the composition of hippuric acid as follows:

$$\underbrace{C_{18} H_9 NO_6}_{\text{Hippuric acid.}} = \underbrace{C_{14} H_6 O_2}_{\substack{\text{Bitter almond} \\ \text{oil.}}} + \underbrace{C_2 HN}_{\substack{\text{Hydrocy-} \\ \text{anic acid.}}} + \underbrace{C_2 H_2 O_4}_{\text{Formic acid.}}.$$
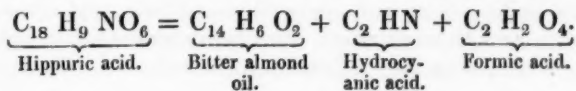
* Ann. Ch. Pharm. LXXX, 17.

This view of its constitution is based principally on the evolution of hydrocyanic acid in the dry distillation of hippuric acid, and on the formation of benzoic acid, carbonic acid, and ammonia, on treating hippuric acid with sulphuric acid and peroxide of manganese.

Since, however, the acids composed of formic acid conjugated with aldehydes (lactic, mandelic acid, &c.) give up the aldehydes in the free state under similar circumstances, it follows that the constitution of hippuric acid assigned by Pelouze, is not in accordance with its decomposition.

After Dessaignes had found that hippuric acid is resolved, by the action of strong boiling acids and alkalies, into benzoic acid and glycocol, the majority of chemists were inclined to regard it as a conjugated compound of those two substances. But upon that supposition, as correctly observed by Berzelius, the transformation effected by peroxide of lead becomes unintelligible.

These different views of the constitution of hippuric acid suppose that there exists in this acid a group of atoms containing 14 equivs. of carbon—that is to say a benzoyl group—together with a second group which contains 4 equivs. carbon, and, under particular circumstances, may be resolved into two other bodies, each containing 2 equivs. of carbon.

Since, however, the nitrogen may be transferred to the one or the other group of atoms, according to the action to which the hippuric acid is subjected, it appears more conformable with the behaviour of this acid, to regard the nitrogen as more intimately combined, not with either of these groups of atoms alone, but with the conjugated compound resulting from their union, and consequently to regard hippuric acid as an amide of the conjugated acid, $C_{18} H_8 O_8$. This acid cannot well be separated by the action of alkalis or acids on the amidogen-acid, because the conjugated acid thereby suffers decomposition. Nitrous acid, however, separates the non-nitrogeneous acid (as previously shown by one of the authors of this paper[*]), acting in fact in this instance as it does upon other amidogen-compounds. To this acid, whose composition is expressed by the formula just stated, the authors give the name of *Benzoglycolic acid.* The present memoir contains a more particular examination of this acid, together with its salts and products of decomposition.

The hippuric acid used in the preparation was obtained from horses' urine, by Gregory's process somewhat modified, viz., by boiling the urine for a short time with milk of lime, then straining the liquid, carefully neutralizing it with hydrochloric acid, concentrating at a boiling heat, and adding hydrochloric acid after cooling. The hippuric acid thus obtained, after being washed with cold water, was nearly white, with only a faint tinge of red.

* Ann. Ch. Pharm. LXVIII, 54.

Hippuric acid does not act upon an aqueous solution of nitrate of potash, neither is any action produced by dissolving it in strong sulphuric acid, and passing nitrous acid (evolved from nitric acid and starch) through the solution.   But when nitrous acid is passed into a warm aqueous solution of hippuric acid in which powdered hippuric acid is suspended, decomposition takes place, attended with evolution of nitrogen.   This method, however, is not advantageous, because a large portion of the nitrous acid is resolved into nitric oxide and nitric acid, which latter substance decomposes the new acid at the temperature of the liquid.   The following method was found to yield the best results.

The hippuric acid, dried in the air and pulverized, was mixed in a mortar with a quantity of commercial nitric acid, sufficient to form it into a thin paste. The mass was then put into a tall glass cylinder (so as to form a long column of liquid), and nitric oxide gas (evolved from copper and nitric acid) passed through it at a moderate rate.   As a strong effervescence takes place, the cylinder must not be more than half filled with the liquid.   The hippuric acid then dissolves, and bubbles of nitrogen are evolved from the liquid.   The termination of the action cannot be very accurately observed, but the passage of the gas may be continued till the liquid assumes a distinct green colour; an excess of nitric oxide is not injurious, but rather beneficial, inasmuch as it removes a portion of the solvent.   The operation is complete in five or six hours, and does not require the application of heat. Part of the benzoglycolic acid separates from the solution even during the passage of the gas, but the greater portion is precipitated on the addition of water.   The liquid, which has become warm, is then left to cool, and filtered through a paper filter doubled at the apex, and the benzoglycolic acid is washed on the filter with water as cold as can be obtained.

The benzoglycolic acid thus produced is impure and has a slight yellow colour.   It is purified by converting it into a lime-salt, and decomposing this salt with hydrochloric acid.   For this purpose, the crude acid is suspended in water, and neutralized with milk of lime. It then solidifies in a few minutes to a solid mass; but on the application of heat, the lime-salt dissolves, and separates out from the filtered liquid on cooling, in very long, fine needles, which are yellow at first, from enclosed mother-liquor, but after washing with cold water, and strong pressure, become perfectly colourless.   The nitric acid diluted with water retains a considerable quantity of benzoglycolic acid in solution.   This portion may be separated by neutralizing with carbonate of potash ; concentrating at a boiling heat ; decanting the liquid from the nitrate of potash which separates out on cooling ; concentrating again ; and mixing this last mother-liquid, which contains nearly all the benzoglycolate of potash, with strong nitric acid. The crystals which separate consist of benzoglycolic acid generally

contaminated with benzoic acid, to remove which, one half of the mixture is neutralized with milk of lime, the other half then added, and the mixture evaporated to dryness. The benzoglycolic acid then remains in combination with the lime, while the benzoic acid is set free and may be dissolved out by ether in Payen's extraction-apparatus. The benzoglycolate of lime which remains is perfectly pure and white.

To obtain the pure acid, the lime-salt is dissolved in water, and mixed in the cold with hydrochloric acid, whereupon the acid separates in the form of a light, perfectly white powder. Larger crystals are obtained by dissolving the lime-salt in alcohol, adding sulphuric acid, filtering, and leaving the liquid to evaporate freely. The acid then separates in tolerably large, colourless prisms, with dihedral angles of 37° 40′ and 142° 20′, and flattened into thin tables by the excessive development of two of the prismatic faces.

The crystals separated from the alcoholic solution lost no weight at 100°; their analysis yielded the following results :

		Calculation.		Mean of experiments.
C_{18}	108	60·00		60·09
H_8	8	4·44		4·66
O_8	64	35·56		35·25
$C_{18} H_8 O_8$	180	100·00		100·00

Benzoglycolic acid is very sparingly soluble in cold water, but dissolves more readily in hot water, by which also it is gradually decomposed. Heated with a quantity of water not sufficient to dissolve it, it fuses into oily drops. It dissolves readily in alcohol and ether. When heated on platinum-foil, it fuses, and solidifies again in the crystalline state in cooling. When strongly heated, it gives off vapours which excite coughing and smell of benzoic acid, leaving a coaly residue which easily burns away at a red heat.

SALTS OF BENZOGLYCOLIC ACID.

These salts are mostly soluble in water, and many of them also in alcohol. They have a neutral reaction and a faint but peculiar taste. From the aqueous solutions, most of the stronger acids, and even acetic acid, throw down benzoglycolic acid in small crystals.

Benzoglycolate of potash is obtained by exactly saturating the acid with carbonate of potash, or by decomposing the lime-salt with carbonate of potash. It dissolves readily in water and alcohol, and crystallizes with difficulty and indistinctly. From a solution saturated while hot, it crystallizes, on cooling, in extremely thin and very broad tables. By spontaneous evaporation, it is obtained in cauliflower-like masses.

Benzoglycolate of soda crystallizes much more readily than the potash-salt, and separates on cooling from a hot saturated solution in tolerably large, rhombic tables, whose composition is: $NaO . C_{18} H_7 O_7 + 6Aq.$ The whole of the water is given off at 100°.

The ammonia-salt is prepared like the potash-salt; it gives off ammonia when evaporated.

Benzoglycolate of lime is obtained, as already described, by saturating the free acid with milk of lime. It possesses in the highest degree, the property of forming super-saturated solutions, so that sometimes, perfectly cold solutions from which part of the salt has already crystallized out, become turbid while being strained through a fine cloth, and in a few minutes solidify to a thick jelly. If the liquid be then filtered, the mother-liquor generally solidifies again after a while. The salt forms fine silky needles grouped like Wavellite. The crystals are permanent in the air, lose no weight at 100°, but give off 1 atom water at 120 °C. Their formula is $CaO . C_{18} H_7 O_7 + Aq.$ 100 parts of water dissolved 2·36 parts of the salt at 11° C., and 13·26 parts at 100°.

Benzoglycolate of baryta crystallizes like the lime-salt in silky crystals. It contains 2 atoms water of crystallization which it gives off at 100°.

Benzoglycolate of magnesia is obtained by mixing the boiling solutions of benzoglycolate of lime and sulphate of magnesia, and exhausting the solidified mass with absolute alcohol. The salt crystallizes by evaporation and cooling in extremely fine soft needles, and consequently forms a very bulky mass.

Benzoglycolate of ferric oxide.—When solution of benzoglycolate of lime is mixed with sesquichloride of iron, a bulky non-crystalline flesh-coloured precipitate is obtained, which becomes darker on the surface when exposed to the air. It is perfectly insoluble in water. When dried in the air, it contains 28 atoms water which are all driven off at 100°. The formula is: $2 Fe_2 O_3 . 3(C_{18} H_7 O_7) + 28 Aq.$

Benzoglycolate of zinc is obtained on mixing the lime-salt with chloride of zinc, in long, thin, colourless needles, grouped in stellate masses. The crystals contain $ZnO . C_{18} H_7 O_7 + 4 Aq.$; the whole of the water escapes at 100°.

Benzoglycolate of copper is obtained by mixing a boiling solution of the lime-salt with nitrate of copper. It crystallizes in beautiful blue rhombic tables, very sparingly soluble in cold water, somewhat more soluble in hot water. On heating the crystals with a quantity of water not sufficient to dissolve them, the undissolved portion is converted into a green powder, probably consisting of the anhydrous salt. At 100° the crystals become green and opaque, but the faces retain their lustre.

Lead-salts.—α. *Sesquibasic.*—A cold solution of benzoglycolate of lime is precipitated in curdy flakes by neutral acetate of lead. The

precipitate is sparingly soluble in cold water; when heated with water, it first melts, then dissolves completely, and separates again on cooling. The first deposit is amorphous, but after cooling the lead-salt separates in crystals. On digesting the original curdy precipitate in a large quantity of cold water, filtering, and leaving the solution to spontaneous evaporation, the salt was obtained after a few days in crystals united in dense, hemispherical masses. These crystals contain 3 atoms water which are given off at 100°, the anhydrous salt fusing at the same time. Their composition is: $3 PbO$. $2(C_{18} H_7 O_7) + 3 Aq.$

β. *Monobasic.*—The mother-liquor from which the preceding salt had separated, yielded after long standing, a quantity of thin, short, soft needles, grouped in stellate masses. These crystals were easily separated from the former salt by levigation. They are anhydrous, their formula being, PbO . $C_{18} H_7 O_7$.

γ. *Sexbasic.*—A boiling solution of the lime-salt, mixed with neutral acetate of lead, yields an amorphous white precipitate, which is almost wholly soluble in acetic acid: it is a mixture of several basic salts. But when a cold solution of benzoglycolate of lime is mixed with basic acetate of lead, a flocculent precipitate is formed which does not fuse when boiled in water, and is but very slightly soluble in water. The precipitate, after partial washing, was immersed in cold water, the solution filtered, and then left to stand. In a few days, crystals were separated, having the appearance of the neutral salt, and mixed with a small quantity of carbonate of lead from which they were separated by levigation. Their composition was found to be: $6PbO$. $C_{18} H_7 O_7 + 2 HO$; the water was given off at 100°. The lead precipitates obtained by direct precipitation are always mixtures of several basic lead-salts.

Benzoglycolate of silver.—When a neutral solution of the lime-salt is mixed with nitrate of silver, the resulting precipitate washed with a small quantity of cold water, then dissolved in boiling water, and the solution left to cool, fine white microscopic crystals are obtained, which soon blacken when exposed to daylight. When prepared by artificial light, the salt is perfectly white. Its formula is: AgO . $C_{18} H_7 O_7$.

Benzoglycolic ether.—An alcoholic solution of benzoglycolic acid left to stand for some time, evolves a peculiar odour, probably arising from the formation of a compound ether. But on passing dry hydrochloric acid into an alcoholic solution of the lime-salt, in which a quantity of the solid salt was suspended, and afterwards adding water, an oily liquid separated which was found to consist almost wholly of benzoic ether; the benzoglycolic acid therefore had been decomposed by the hydrochloric acid.

From the preceding description of the salts of benzoglycolic acid,

it appears that this acid, $HO . C_{18} H_7 O_7$ contains 1 equiv. of water which can be replaced by metallic oxides, and moreover saturates the same quantity of base as the hippuric acid from which it is produced. Its production from hippuric acid is expressed by the equation :

$$\underbrace{C_{18} H_9 NO_6}_{\text{Hippuric acid.}} + NO_3 = \underbrace{C_{18} H_8 O_8}_{\text{Benzoglycolic acid.}} + HO + 2N,$$
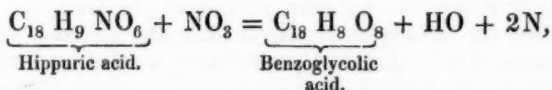
and is therefore perfectly analogous to the formation of other acids from their amides. The saturating power is, however, remarkable; for in most cases the amidogen-acid saturates 1 equiv. of base less than the free acid. Nevertheless the case of benzoglycolic acid is not quite peculiar; for the same relation is observed between aspartic acid and malic acid produced from it by a reaction similar to the above,* also between salicylic acid and its amide.

This saturating power shows a remarkable difference between the ordinary amides and amidogen-acids, and the bodies which stand nearest to this group, viz., hippuric acid, alanin, anthranilic acid, &c. though both exhibit the same deportment towards nitrous acid.

PRODUCTS OF DECOMPOSITION.

It has been already mentioned that benzoglycolic acid is generally decomposed by boiling its aqueous solution with water; its salts are also decomposed in the same manner, but much more slowly. The acid is much more quickly decomposed when heated with dilute acids, benzoic acid volatilizing with the watery vapours, and a new acid remaining in solution.

To examine this new product, benzoglycolic acid was boiled for some days with water to which a small quantity of sulphuric acid was added, the water being replaced as it evaporated. A large quantity of benzoic acid volatilized with the watery vapour, and on concentrating to a small bulk and leaving the solution to cool, a further quantity of that acid crystallized out. The mother-liquor was neutralized with carbonate of baryta, filtered from the precipitated sulphate, evaporated to a syrupy consistence, and left to stand for several days. A salt then separated in white hard crystalline crusts, which gave by analysis results nearly agreeing with the formula :

$$BaO . C_4 H_3 O_5.$$

The acid contained in this salt, which in the anhydrous state has the formula $C_4 H_3 O_5$, or in the hydrated state, $\overset{\cdot}{C}_4 H_4 O_6$, agrees

* Ann. Ch. Pharm. LXXV, 296.

with that to which Laurent* assigns the name of *Glycolic acid*, because glycocol may be regarded as its amide.

$$\underbrace{C_4\,H_4\,O_6}_{\text{Glycolic acid.}} + NH_3 = \underbrace{C_4\,H_5\,NO_4}_{\text{Glycocol.}} + 2\,HO.$$
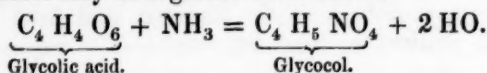
This acid, however, had not been previously prepared.

To separate the acid from its baryta-salt, the aqueous solution of that salt is treated with dilute sulphuric acid, filtered, and the filtrate evaporated over the 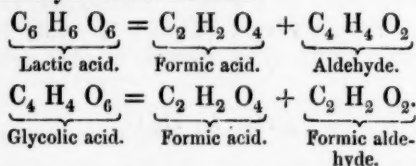water-bath. The syrupy residue dissolves completely in ether, and on evaporating the ether, the acid is again obtained in the form of a thin syrup which refuses to crystallize.

Glycolic acid is miscible in all propertions with water, alcohol and ether. It has a strongly sour taste, and does not give a precipitate with any metallic salt. In all its properties it bears the closest resemblance to lactic acid; indeed, the only reaction which distinguishes the two is, that when a solution of glycolic acid is mixed with acetate of lead, and ammonia added, a white flocculent precipitate is produced, whereas lactic acid similarly treated remains clear.

Glycolate of zinc was obtained by heating the diluted aqueous acid with carbonate of zinc, then filtering and evaporating. As the liquid cooled, crystalline crusts separated out, having a strong resemblance to lactate of zinc. The individual crystals are small, colourless, transparent prisms, arranged in stellate groups round numerous points. The formula of the salt is $ZnO \cdot C_4\,H_3\,O_5 + 2\,Aq$. The water is given off at 100°. The salt is insoluble in alcohol, difficultly soluble in cold water, more readily in hot water. 1 part of the anhydrous salt dissolves in 33 parts of water at 20° C.

Glycolate of silver appears to be a very instable salt. The solution obtained by decomposing glycolate of baryta with sulphate of silver and filtering, decomposed and deposited a black insoluble substance, even when evaporated in vacuo over sulphuric acid. The addition of alcohol or of ether to the solution produced no precipitate.

Glycolic acid, as already observed, exhibits an extremely close resemblance to lactic acid. If the latter may be regarded as a conjugated compound of formic acid with common aldehyde, glycolic acid ought perhaps to be considered as a corresponding compound containing the aldehyde of formic acid:

$$\underbrace{C_6\,H_6\,O_6}_{\text{Lactic acid.}} = \underbrace{C_2\,H_2\,O_4}_{\text{Formic acid.}} + \underbrace{C_4\,H_4\,O_2}_{\text{Aldehyde.}}$$

$$\underbrace{C_4\,H_4\,O_6}_{\text{Glycolic acid.}} = \underbrace{C_2\,H_2\,O_4}_{\text{Formic acid.}} + \underbrace{C_2\,H_2\,O_2}_{\substack{\text{Formic alde-}\\\text{hyde.}}}$$

Formic aldehyde is probably obtained in the dry distillation of glycolic acid, or on treating that substance with oxidizing agents.
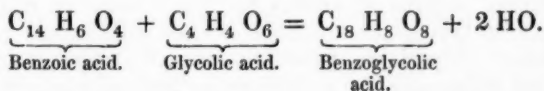
* Ann. Ch. Phys. [3], XXIII, 112.

When hippuric acid is treated with peroxide of lead, an extremely pungent odour is evolved; and Schwartz observed that the aqueous distillate gives the reactions of the aldehydes with nitrate of silver. It seems therefore probable that these phenomena are produced by the aldehyde of formic acid, which, being gaseous at ordinary temperatures, has hitherto escaped notice.

Glycolic acid is also produced by the action of nitrous acid upon glycocol. This substance, in the state of aqueous solution, is decomposed by nitrous acid, with evolution of nitrogen. If the solution be then evaporated, the glycocol becomes oxidated by the nitric acid produced from the nitrous acid, and crystals of oxalic acid are found in the residue. If on the other hand, the solution of glycocol, after treatment with nitrous acid, be agitated with ether, the ether extracts the glycolic acid from the aqueous solution; and, on evaporating the ether, the glycolic acid remains in the form of a syrupy liquid, similar in properties to the acid obtained from benzoglycolic acid. The preparation from the last-mentioned acid is however the easier method of the two. The formation of glycolic acid from glycocol is expressed by the equation :

$$\underbrace{C_4\,H_5\,NO_4}_{\text{Glycocol.}} + NO_3 = \underbrace{C_4\,H_4\,O_6}_{\text{Glycolic acid.}} + HO + 2\,N.$$
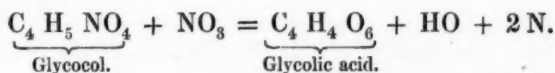
The same results are therefore obtained whether hippuric acid be first treated with nitrous acid and the benzoglycolic acid afterwards decomposed by boiling with acids, or the hippuric acid first resolved into benzoic acid and glycocol, and the latter subsequently treated with nitrous acid.

It appears, from the facts already stated, that benzoglycolic acid is easily resolved into benzoic and glycolic acids, and there are grounds for supposing that it may be reproduced by the union of its constituents : thus

$$\underbrace{C_{14}\,H_6\,O_4}_{\text{Benzoic acid.}} + \underbrace{C_4\,H_4\,O_6}_{\text{Glycolic acid.}} = \underbrace{C_{18}\,H_8\,O_8}_{\substack{\text{Benzoglycolic}\\\text{acid.}}} + 2\,HO.$$

The authors were prevented by want of material from confirming this theory by experiment, but they obtained an analogous result with lactic acid. A mixture of lactic and benzoic acid was heated to 180° C., and kept at that temperature as long as aqueous vapour continued to escape. The residue solidified, on cooling, in a resinous mass which was dissolved in water with addition of potash. To the warm solution, dilute sulphuric was added, till benzoic acid no longer crystallized out on cooling, and the crystals obtained exhibited a different form. The separated acid was then removed by filtration, and the filtrate mixed in the cold with dilute sulphuric acid. An abundant precipi-

tate was produced, which first fused on being boiled with water, then dissolved in a large quantity of water, and on cooling separated partly in drops, partly in crystals. This acid was dissolved in ether and recrystallized by evaporation, then neutralized with ammonia, and precipitated by silver-solution, The precipitate yielded 39·7 per cent of oxide of silver, a result nearly agreeing with the formula, AgO . $C_{20} H_9 O_7$, which requires 38·5 per cent. The excess arose from the presence of benzoic acid. The formation of the new acid, which may be called *Benzolactic acid*, is expressed by the following equation :

$$\underbrace{C_{14} H_6 O_4}_{\text{Benzoic acid.}} + \underbrace{C_6 H_6 O_6}_{\text{Lactic acid.}} = \underbrace{C_{20} H_{10} O_8}_{\substack{\text{Benzolactic}\\ \text{acid.}}} + 2 HO.$$
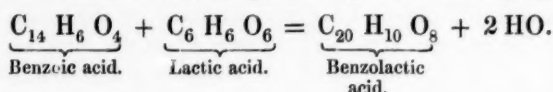
On a new method of separating substances possessing very similar propertics.

By W. Heintz.[*]

This method is founded on an extension of the principle applied by Liebig[†] to the separation of certain volatile acids of the adipic series. It consists in adding to the mixture a substance capable of combining with all the original substances which compose it, but in quantity less than sufficient to saturate the whole, and subjecting the mixture thus treated to distillation, the action of solvents, &c.

In order that a separation may be effected in this manner, it is necessary; first, that the substance added possess a decided chemical affinity for the substances contained in the mixture, and that the resulting compounds differ so much in their properties from the original substances, as to be easily separated from them by the action of solvents or by distillation ; secondly, that the substance added possess different degrees of affinity for the substances contained in the mixture. If this latter condition be not fulfilled, no separation can take place. Experience shows, however, that perfect equality of affinity of two substances for a third exists only at particular temperatures ; hence, by varying the temperature, the desired inequality may always be attained.

The particular mode of effecting the separation will of course vary with the nature of the substances present. The following is the process which the author has adopted with mixtures of the non-volatile fatty acids, stearic, margaric acid, &c. The separation of these bodies is well known to be a matter of great difficulty, on account of the close resemblance existing between them and all their corresponding compounds.

* Pogg. Ann. LXXXIV, 221.   † Ann. Chem. Pharm. LXXI, 325.

The fatty acids are dissolved in a quantity of boiling alcohol, sufficient to retain the whole in solution when the temperature is lowered to 0° C., and a boiling alcoholic solution of crystallized acetate of lead is added drop by drop, in quantity sufficient to saturate about one-half of the acids with oxide of lead. In most cases, as with stearic, margaric, ethalic, and palmitic acid, the quantity of sugar of lead required for this purpose amounts to about one-third of the weight of the fatty acids. If the proper quantity of alcohol has been added to the mixture, the alcoholic solution remains clear as long as it is kept boiling, but becomes turbid on the slightest reduction of temperature; and as the liquid cools, the whole of the oxide of lead is precipitated in combination with half the fatty acid. The formation of a precipitate at the boiling temperature shows that the quantity of alcohol used is insufficient; in that case it is best to add a few drops of acetic acid, by which the separated lead-salt is readily dissolved. The liquid is filtered when cold, and the precipitate washed till the filtrate is no longer clouded by water; the washing is very expeditious.

The lead-salt, saturated with alcohol, is then removed from the filter and boiled for a short time with hydrochloric acid. Chloride of lead then separates completely, and sinks rapidly to the bottom, while the fatty acid remains dissolved in the alcohol. The solution, however, still contains a portion of the ethyl-compound of the fatty acid. It is therefore super-saturated with caustic potash, and boiled till the ethyl-compound is completely decomposed; after which, water is added, and the greater part of the alcohol expelled by evaporation. Lastly, the acid is separated from the potash-salt by boiling with hydrochloric acid.

To separate the acid dissolved in the alcoholic solution, acetate of lead also dissolved in alcohol is added in slight excess, the precipitate collected on a filter, and treated in the manner already described.

As the separation thus effected is not complete, the lead-precipitates, instead of being washed, may be squeezed by a powerful press, and then decomposed by boiling with very dilute hydrochloric acid, or better, by treating them with alcohol and hydrochloric acid and afterwards with hydrate of potash and hydrochloric acid. The melting points of both portions of the acid are then to be determined. If they are nearly equal, and the two portions are otherwise not essentially different in their physical properties, it may safely be concluded that the substance under examination was not a mixture, but consisted essentially of *one* definite compound, possibly contaminated by a small quantity of another. In this case, the two portions may be united, and purified by one or two recrystallizations from alcohol. If, on the contrary, the melting points and other physical characters of the two acids differ considerably, the process must be repeated upon each, and the same treatment continued till the melting

G 2

points, &c. of the portions last separated are nearly equal. These last portions are then to be united and crystallized once or twice from alcohol. This process will serve likewise to separate a mixture of three or more acids, provided that not only the extreme portions, those namely which contain the strongest and weakest acids, but likewise the intermediate portions, are subjected to the same treatment.

If any of the acids thus separated assume a well-defined crystalline structure, when it passes from the liquid to the solid state, it will for the most part be unnecessary to subject it any further to the preceding treatment; one or two crystallizations from alcohol will yield it in a state of perfect purity.

When it is thought that a pure acid has been obtained in the manner above described, it is best to subject it once more to the same treatment, in order to make sure of its purity.

By pursuing this method the author has found:

1. That the so-called pure *stearine* which melts at 61° or 62° C., is a mixture of two or more fats containing glycerine.

2. That the substance commonly regarded as pure *cetine* is a mixture of at least two fats containing ethyl. It does not melt constantly at 49° or 49·5° C.; but by recrystallization from the ethereal solution, its melting point may be raised to 53·5°.

Another result of the author's experiments is, that spermaceti may be easily saponified by a boiling solution of caustic potash.

On the composition of Human Fat.

By W. Heintz.

The investigations of Chevreul into the composition of human fat showed, that it consists of a liquid fat, viz., oleine, and a solid fat, to which Chevreul gave the name of stearine, but which, as it yields margaric acid by saponification, must really consist of margarine. Subsequently Lerch has shown that the volatile portion of the fat contains caprylic acid; and Brücke, has found that the solid portion does not yield pure margaric acid by saponification, but an acid which melts at 56°, and does not crystallize like margaric acid.   Hence it would appear that human fat contains besides margarine, another solid fat which by saponification yields another fatty acid, not separable from margaric acid by crystallization.

After various fruitless attempts to obtain the pure margarine by exposing the fat to a very low temperature, and crystallizing the solid portion from a solution in ether, Heintz resorted to the method of

saponifying the fat with caustic potash; and as the separation of the oleic acid thus produced from the margaric and other solid acids, by the usual method of converting them into lead-salts and digesting in ether, is very tedious and involves a very large consumption of ether, he finally adopted the method of separating the fatty acids from the mixed potash-salts by means of hydrochloric acid, and subjecting the liquid portion to the action of powerful press,—then dissolving the resulting hardish mass in a third of its weight of alcohol, leaving it to solidify at as low a temperature as possible, pressing again, and repeating these operations till every trace of oleic acid was removed from the solid acids—a point which was generally attained at the third pressure. The mixture of solid fatty acids was then treated by the method described in the preceding paper, and was found to contain four different fats. The liquid portion was found to consist principally of oleine. The general results of the investigation are as follows :

1. Human fat does not consist, as formerly supposed, merely of oleine and margarine, but is a mixture of at least *six* different fats.

2. The first of these fats is present in very small quantity only, but appears, from an analysis of the fatty acid obtained from it, to be identical with *Stearophanine,* the substance which Francis discovered in the berries of *Cocculus indicus.* The composition and properties of this acid, so far as they have been studied, agree with those of stearophanic acid, the formula of which is $C_{36} H_{36} O_4$.

3. The second fat is a new substance, to which the author gives the name of *Anthropine.* The fatty acid obtained from it by saponification, is distinguished by its strong tendency to crystallize. It separates from the alcoholic solution, and likewise solidifies from a state of fusion, in broad, shining laminæ. Its composition appears to agree with the formula, $C_{34} H_{32} O_4$; but further experiments are necessary to establish this result.

4. The third fat is *Margarine,* which yields margaric acid by saponification.

5. The fourth substance contained in this solid portion of the fat is *Palmitine,* which yields palmitic acid by saponification; it appears to be the most abundant of the four.

6. The palmitic obtained from human fat is identical with that which is formed by the action of fused potash upon oleic acid, and to which Varrentrapp gave the name of *Olidic acid.*

7. The liquid portion of human fat is composed essentially of *Oleine;* but it likewise contains a small quantity of another fat, which, by saponification, yields an acid whose baryta-salt differs from oleate of baryta, not only by its physical properties, but likewise by the quantity of baryta contained in it, viz., from 27 to 28 per cent. This baryta-salt is much less soluble in alcohol than oleate of baryta, but

is converted into a tenacious liquid mass at a much lower tempera-
ture than the latter, and is more soluble in ether.

8. It has been before observed that when human fat is exposed in
water to a temperature varying above and below $0°$ C., a liquid fat
may be separated from the solid portion; and this liquid fat, if left to
itself till the next winter, and again exposed for some time to the
same low temperature, yields another tolerably large portion of solid
fat. If this be again separated by pressure, and the liquid fat once
more left to itself, a still further portion of solid fat will separate in
the following winter. Now, when the solid fat thus separated in the
second or third winter, is dissolved in hot alcohol, filtered when the
temperature of the liquid has fallen to $30°$ C., and then left to cool
further, a substance separates out, which, after recrystallization from
alcohol, dissolves readily in a dilute aqueous solution of carbonate of
soda at a boiling heat, and therefore consists of a fatty acid. It
appears then that human fat when left to itself, undergoes a gradual
decomposition, by which the glycerine is destroyed, and the fatty
acid separated, a kind of decomposition long known to take place in
fats which yield easily volatile acids, for instance, in butter when it
becomes rancid.

On a new compound of Mercury.

By Sobrero and Selmi.[*]

When an alcoholic solution of potash is added to a solution of
corrosive sublimate in alcohol of the strength of $40°$, a yellow preci-
pitate is obtained, consisting, not of protoxide of mercury, but of a
compound of mercury with carbon, hydrogen, and oxygen. This
precipitate is amorphous and insoluble in water and alcohol; it may
be washed to free it from excess of potash and chloride of potassium.

In preparing this substance, it is best to employ a temperature of
about $50°$ C. It is stable at ordinary temperatures, and sustains
without decomposition a temperature not far from $200°$ C.; when
more strongly heated, it assumes an orange colour, and decomposes
suddenly and with violent detonation, being completely resolved into
gaseous products without residue. That the compound may possess
the property of detonating in the manner just described, the prepara-
tion must be conducted with attention to the circumstances above-
mentioned; if the preparation be made at a lower temperature, or an
insufficient quantity of potash added, the resulting precipitate deto-
nates less strongly and leaves a residue of red oxide of mercury.

* Compt. Rend. XXXIII, 67; Ann. Ch. Pharm. LXXX, 108.

When exposed to direct light, this body blackens very rapidly. If heated in a glass tube while still moist, it decomposes with less violence and leaves metallic mercury, water, and acetic acid.

This substance dissolves completely in hydrochloric acid, even in the cold, undergoing decomposition at the same time, and yielding a volatile substance, which has a pungent, irritating, and quite peculiar odour, and acts upon the throat in a similar manner to hydrocyanic acid. This volatile substance may be obtained, mixed with hydrochloric acid, by distilling the mixture. The authors have not yet analyzed this substance; but they observe that, on the addition of nitrate of silver, there is formed, besides the precipitate of chloride of silver, a soluble compound which yields very beautiful, transparent crystals.

Sulphuric acid dissolves this compound of mercury, forming crystalline products. Nitric acid likewise dissolves it, and the solution yields with caustic potash, an ash-grey precipitate, which when treated with hydrochloric acid, gives off a volatile substance having the same odour as that produced when the original mercury-compound is acted upon by hydrochloric acid. Acetic acid dissolves the mercury-compound almost completely, and the solution, when evaporated, yields a crystalline substance.

The new mercury-compound boiled with a solution of sal-ammoniac, drives out the ammonia, forming, at the same time, a soluble, crystallizable body. A crystalline compound is likewise obtained by boiling that substance with a solution of corrosive sublimate.

Although the authors have hitherto been unable to obtain any determinate data for the composition of this remarkable compound, they are nevertheless able to assert that it consists of mercury, carbon, hydrogen, and oxygen, and that the last three elements are not in the proportion required to form alcohol, the quantity of hydrogen being much too small; moreover, that the compound acts like a very strong base, and combines, not only with sulphuric, nitric, and acetic acid, but likewise with many other acids.

In the course of the experiments made with this substance, other mercury-compounds were obtained having more or less relation to it. Thus a substance different from the preceding is obtained by slowly adding a very weak solution of potash to a boiling solution of corrosive sublimate, &c.

On dissolving mercury in nitric acid, expelling all nitrous products by continued boiling, and adding the solution to alcohol of 36°, in the same proportion as for the preparation of fulminating silver, no immediate action takes place, provided the mixture be made at a temperature below 100°; but if the temperature be raised to 100°, a white crystalline compound is instantly formed, and its formation continues, even when heat is no longer applied. This reaction, not-

withstanding the rapidity with which it goes on, is not attended with evolution of gas. The precipitate contains mercuric oxide, nitric acid, carbon and hydrogen ; when treated with hydrochloric acid, it yields a volatile product having the peculiar odour mentioned in a former part of this paper.

It may be confidently predicted that compounds analogous to the above will be obtained by similar processes, in which amylic or methylic alcohol is used instead of common alcohol, and other metals, such as silver, instead of mercury.

On Ethylo-mercuric Nitrate.

By Ch. Gerhardt.[*]

Gerhardt did not succeed in preparing the yellow detonating oxide of mercury by the process described by Sobrero and Selmi;[†] he is moreover of opinion that this process is not likely to yield a product sufficiently pure for analysis. On the other hand, he readily obtained the peculiar salt produced on mixing alcohol with mercuric nitrate. This salt has a very remarkable constitution, as will be seen by the following observations.

Mercurous nitrate has no action on alcohol. When an acid solution of that salt is mixed with alcohol of 36°, and the mixture heated, basic mercurous nitrate separates out in white crystals, which do not contain organic matter.

When alcohol is mixed with a very concentrated solution of mercuric nitrate, there is formed in the cold, an amorphous white precipitate of basic mercuric nitrate; if the mercury-salt contains excess of nitric acid, no precipitate is formed in the cold. On heating the liquid, however, a white crystalline precipitate separates, even before the liquid begins to boil, and its formation continues, without further application of heat. This is the salt obtained by Sobrero and Selmi. When examined by the microscope, it exhibits a highly characteristic form, consisting of six-pointed stars or hexagonal tables, which are shaded in such a manner that similar stars appear within them, whose vertices project into the angles of the tables.

The salt is insoluble in water and in alcohol. When heated in a small tube, it decomposes suddenly and explosively, but does not detonate.
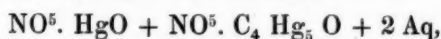
After drying over sulphuric acid, the composition of the salt was found to be as follows :
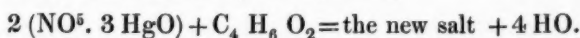
		Calculation.		eri	me nt.	
C_4	24	3·1	2·7	2·9	2·9	
H_2	2	0·3	0·4	0·3	0·3	
Hg_6	600	78·3	78·4			
N_2	28	3·3	3·6			
O_{14}	112	15·0				
	766	100·0				

These numbers agree with the formula,

$$NO^5 . HgO + NO^5 . C_4 Hg_5 O + 2 Aq,$$

which formula is conformed by the equation,

$$2 (NO^5 . 3 HgO) + C_4 H_6 O_2 = \text{the new salt} + 4 HO.$$

That this salt is a mercuric and not a mercurous salt, is shown by its property of dissolving completely in hydrochloric acid, without leaving a trace of calomel; it evolves, however, when thus treated, the peculiar odoriferous substance mentioned by Sobrero and Selmi. The solution in hydrochloric acid is precipitated yellow by potash.

When a strong solution of potash is poured upon the new salt, it turns grey; by boiling with the same solution, it turns black, without however being completely decomposed. The black substance is always mixed with crystals, however long the boiling may be continued. This black substance is not dissolved by hydrochloric acid, although but a small quantity of calomel is formed. It follows therefore that the salt is essentially altered by the action of potash.

Ammonia acts upon it in a similar manner.

A large quantity of mercurous nitrate is likewise found in the alcoholic solution from which the new salt has separated. A mercurous salt frequently separates in small needles after the new salt has been removed by decantation. The formation of mercurous salt probably depends upon secondary actions, for the mixture of alcohol and corrosive sublimate gives off a strong odour of aldehyde when heated, even though the action is not accompanied by any evolution of gas.

The new salt is acted upon by sulphuretted hydrogen, sulphide of mercury being formed, and likewise a body having the characteristic odour of mercaptan. Hence, in determining the mercury, the organic matter must be first destroyed by boiling the salt with aqua-regia, then evaporating to dryness, and digesting the residue in water. If this precaution be neglected, the mercury will come out 1 or 2 per cent too much, the sulphide collected on the filter being in fact impure.

The composition of the new salt leads to the supposition that the detonating oxide discovered by Sobrero and Selmi, is an oxide of

mercuric ethyl, that is, alcohol in which the hydrogen is replaced by mercury, $C_4 Hg_6 O_2$. Here then we have another instance of the striking analogy which exists between the products of the action of alcohol and of ammonia, that is to say, between the ethers and the amides. We know, indeed, that the ammoniacal oxide of mercury likewise detonates and forms characteristic salts.

On the Allotropy of Selenium.

By Dr. Hittorff.*

Our knowledge of the thermic relations of selenium is due to Ber-zelius, whose statements, as given in his treatise, have been copied without alteration into other compendiums of chemistry; they are as follows:

" Selenium becomes soft when heated, is semi-fluid at 100°, and fuses at a temperature a few degrees higher. During cooling, it remains soft for a long time, and may be drawn out like sealing-wax, into threads, which appear ruby-red by transmitted light. When solidified, it assumes a specular surface, exhibits perfect metallic lustre, and is altogether not unlike blood-stone. Its fracture is con-choidal and vitreous. When fused selenium is left to cool very slowly, its surface becomes uneven, granular, lead-grey, and no longer specular. The fracture is fine-grained, dull, and exactly re-sembles that of a lump of metallic cobalt. A second fusion followed by rapid cooling destroys this appearance, and restores to selenium its original external characters."

A fact observed by the author of this memoir places the relation between crystalline and amorphous selenium in its true light, and shows that the preceding statements require correction. He finds, namely, that granular selenium does not fuse till heated to 217° C., and that it then passes at once from the solid to the liquid state without previous softening. When cooled in the ordinary way, the fused mass does not return to the solid state at this temperature, but remains liquid, and passes through all degrees of softness, till, at a temperature below 50° C., it gradually hardens into amorphous selenium. On plunging the bulb of a thermometer into fused sele-nium heated above 220° C. in a small crucible, the temperature was found to fall quite regularly during cooling. There was no stoppage or retardation. The latent heat absorbed during the fusion of crys-talline selenium is therefore not given up under these circumstances, but remains in the amorphous selenium, and is essential to that state. At lower temperatures, this condition of the selenium is stable.

* Pogg. Ann. LXXXI, 214.

Pieces of fused amorphous selenium, which the author has had in his possession for several years, have remained unaltered. The passage to the crystalline state, takes place, however, on exposing the amorphous selenium for a time to a temperature between 80° and 217° C., the latent heat being at the same time evolved.

In these experiments, an oil-bath was used consisting of three concentric copper cylinders. By means of a spirit-lamp of constant level and a stirrer, the oil of the inner vessel could easily be maintained for any length of time at a constant temperature. The amorphous selenium was placed at the lower part of a common test-tube, and fused round the bulb of a thermometer. The test-tube being introduced through an opening in the cover into the oil of the bath, in which a second thermometer is placed, the thermometer in the selenium soon takes the temperature of the medium, but instead of remaining at that temperature, quickly rises above it. By the time that it has returned to the temperature of the oil-bath, the amorphous selenium, on being taken out, is found to have assumed the granular condition. In amorphous selenium therefore, we have a substance, which, under these circumstances, softens when heated, then becomes semi-fluid, and afterwards returns to the solid state.

The conversion into the granular modification takes place most quickly, and the thermometer rises most above the temperature of the oil-bath when the latter is between 125° and 180°. With a quantity of selenium weighing about 20 grms., the thermometer usually rose from 40° to 50° above the temperature of the oil. The return to the latter temperature takes place very quickly.

A still greater rise of temperature is attained by using, instead of the oil-bath, an air-bath, which conducts away the heat less quickly. A convenient arrangement for the purpose is an ordinary drying apparatus, consisting of a copper cylinder having two apertures in its cover, so that a thermometer may be introduced through one of them, and the test-tube with the amorphous selenium and the second thermometer through the other. If now the cylinder be heated with a small spirit flame which raises the temperature to about 130° C., the naked thermometer rises at first, above that immersed in the selenium. But as soon as the latter has risen to 125°, it begins to mount rapidly, and soon attains a temperature between 210° and 215°.

The process of transformation is slower as the temperature of the bath is farther below 125°. The rise of temperature is then smaller, but continues longer. In the vapour of boiling water the process takes several hours, if the quantity be somewhat considerable; at 80°, it lasts much longer; in both these cases, the evolution of heat is imperceptible. The time required for the transformation depends greatly on the mobility of the particles. If the amorphous selenium

be not fused, but in the state of powder, it assumes the crystalline form so rapidly at 100°, and even at 90°, that the immersed thermometer rises from 25° to 30°. At 80°, in the vapour of ordinary spirit of wine, the rise of temperature is imperceptible even in this case. The greater the fluidity of the amorphous selenium, the more readily does it give up its latent heat. From this cause, the transformation takes place more slowly at temperatures above 180°, because the temperature of the selenium can never rise above 217°, the melting point of the crystalline variety. The latter can only be accurately observed by means of the oil-bath. For this purpose, the bath is kept at a constant temperature of more than 220°, and the crystalline selenium, together with the thermometer, immersed in it. The thermometer soon rises to 217°, then remains stationary for a long time between 217° and 218°, and finally attains the temperature of the oil. The selenium is then found to be melted.

On taking a general view of the thermic relations of selenium, it is impossible to overlook its strong resemblance to sulphur. It is well known, that the latter is obtained in a soft plastic state, by heating it above 250°, and then cooling it as quickly as possible, which is usually effected by pouring it into cold water. It then remains soft for a long time at the lower temperature, and returns but slowly to the crystalline state. This transformation, however, takes place quickly, as observed by Regnault,* if the sulphur be exposed to a temperature higher than the boiling-point of water. At the same time, an appreciable rise of temperature takes place; the thermometer immersed in the sulphur rises to 111°, the temperature of the medium being 98°.

The latent heat absorbed by sulphur heated to 250°, is unable to escape during the short time in which it cools; at a lower temperature it becomes more permanent, and requires several days to escape. It may possibly become quite stable at a still lower temperature at which the soft surface hardens. In the case of selenium, the latent heat takes a still longer time to escape, the time occupied in ordinary cooling, being in fact, insufficient for the purpose. At temperatures below 80°, the selenium hardens, retaining its latent heat, and the condition thus assumed is perfectly stable. Moreover, selenium not only retains that latent heat at ordinary temperatures, but under favourable circumstances, readily absorbs it. It is well known that selenium is obtained in the form of a red powder, when it separates from its compounds or solutions at ordinary temperatures. Thus, sulphurous acid, protochloride of tin, zinc, and iron, throw down red selenium from selenious acid; and seleniuretted hydrogen water deposits red selenium on exposure to the air. Both amorphous and crystalline selenium are dissolved by strong oil of vitriol at

* Pogg. Ann. LIII, 266.

40° C., and the green liquid when mixed with water, deposits red
selenium. This red selenium, however, is nothing more than amor-
phous selenium in a state of minute division; for the latter also
appears red in thin films by transmitted light, and gives a red streak.
The red precipitate turns black when it is heated above 50°, softening
at the same time, and agglomerating into a shining vitreous mass.
Lastly, Count Schaffgotsch found the specific gravity of red sele-
nium the same as that of fused amorphous selenium. Thus, the
density of red selenium was found to be 4·259, and after aggregation
4·264, and that of the glassy modification 4·276—4·286, while that
of granular selenium was 4·796—4·805 at 20° C. Precipitated sele-
nium likewise gives out heat when it passes into the granular state.
In the aggregated form it is the most convenient for this experi-
ment; because it can then be easily pounded, and dried in vacuo over
sulphuric acid. If it be then held in the vapour of boiling water, the
thermometer rises, during the transformation, 125°—130°. Finely-
divided red selenium gives off its water very slowly at ordinary tem-
peratures; the author did not succeed in drying it completely. If
exposed to the direct rays of the sun, it gradually becomes crystalline.
To observe the escape of heat, it is best to apply a temperature of
80°, such as that afforded by the vapour of ordinary spirit of wine;
at this temperature the transformation is very rapid.

Selenium is not always separated from its compounds in the amor-
phous state at ordinary temperatures. The solutions of selenide of
potassium and selenide of ammonium, when exposed to the air, always
deposit it in the crystalline form. The crusts which form on their
surface are entirely made up of small crystals, which appear very
distinct and definite under the microscope; their specific gravity at
15° C. is 4·808.

Vitreous and crystalline selenium differ greatly in their electrical
conducting power. The former is known to be an insulator. Granular
selenium conducts much better, and, which is very remarkable, its
resistance is considerably diminished by heat. Two small plates of
carbon were immersed in melted selenium contained in a crucible,
and the amorphous mass brought into the crystalline state by exposing
it to a temperature of 140° in the drying apparatus. It was then
introduced, together with a galvanometer, having 200 turns of wire
and an astatic needle, into the circuit of a single pair of Grove's
battery. While the selenium was in the amorphous state, no deflection
was produced upon the needle under these circumstances; but after
the transformation into the crystalline modification, a deflection of
17° was produced at ordinary temperatures. On raising the tem-
perature, the deflection increased still further, and at 210° C. it
amounts to 80°. If this increase of conducting-power were to con-
tinue, the selenium when raised to a red heat, would conduct as well

as the ordinary metals; but after the absorption of the latent heat at 217°, the needle suddenly returns to 20°.

The allotropic states of sulphur and selenium are brought about by latent heat. The same cause probably produces similar effects in other bodies, although the relations are not so simple as those above considered.

The author is of opinion that Schrötter's red phosphorus is formed in a similar manner, viz., by the abstraction of latent heat from ordinary phosphorus, and that it is really the crystalline modification of the body, ordinary colourless phosphorus being the amorphous variety. It is true, that no crystalline structure has been detected in the red phosphorus; but on the other hand, it is always obtained either in a state of very minute division, or somewhat aggregated in crusts, conditions not very favourable to the observation of its structure.

On Phosphide of Tungsten.

By Wöhler.[*]

Phosphorus and tungsten combine directly, but without emission of light and heat, when finely-pounded metallic tungsten contained in a glass tube is heated to redness in phosphorus vapour. The resulting compound is a dull, dark grey powder, very difficult to oxidize, and composed according to the formula $W^3 P^2$. This formula requires 18·7 per cent of phosphorus; two experiments gave 18·38 and 18·87.

Much more remarkable is the phosphide of tungsten obtained by reducing a mixture of tungstic and phosphoric acids, at a very high temperature, in a crucible lined with charcoal. In this manner a compound is obtained, crystallized in magnificent geodes, having exactly the appearance of certain geodes filled with crystals, which occur in the mineral kingdom. The production of this beautiful arrangement was not the result of a single accident, but was repeated in four different experiments. In every case, there was formed a hollow mass of grey coke-like phosphide of tungsten, several inches high, more than an inch wide, corresponding to the dimensions of the crucible, and lined internally with the most brilliant crystals, many of which, though they were very thin prisms, attained a length of nearly an inch. They have a steel grey colour, and an exceedingly brilliant metallic lustre. They are six-sided prisms, apparently identical in form with gypsum. Their spec. grav. is 5·207. They

are perfect conductors of the electric current. When treated with zinc and dilute acid, they liberate hydrogen gas, and when immersed in a solution of a copper-salt they become covered with metallic copper.

This phosphide of tungsten undergoes no change when heated to the melting-point of manganese. It likewise remains nearly unaltered when heated to redness in the air. Heated on charcoal in a stream of oxygen gas, it burns with great splendour; and forms a deep blue sublimate on the charcoal. It likewise burns with an equally dazzling lustre on fused chlorate of potash. It is not attacked by any acid, not even by aqua-regia.

The proportion of phosphorus in this compound was found by three experiments to be 7·87, 8·70 and 8·78. The formula $W^4 P$ requires 8 per cent.

For the preparation of this very beautiful substance, crude phosphoric acid containing lime, and fused in an earthen crucible, was generally used; it was mixed in coarse powder with the tungstic acid, and generally in the proportion of 2 equivs. $PO^5 : 1\ WO^3 = 9·7$. The quantity of tungstic acid used in each experiment was between 20 and 30 grms. The mixture was exposed in the charcoal crucible to a heat sufficient to keep nickel in a state of perfect fusion. In this manner, the largest and finest crystals were obtained, but the surrounding crust of phosphide of tungsten was intimately mixed with fused particles of slag, which could not be removed by any solvent. A less beautiful product was obtained by the use of pure phosphoric acid; but in this case also the remarkable formation of the hollow geode-space and the crystallization on its sides were exhibited. The formation of these crystals, which project freely and often perfectly isolated into the hollow, probably takes place in the liquid phosphoric acid, which at first remains undecomposed in the interior of the mass, and afterwards, being gradually reduced to the state of phosphorus, volatilizes, leaving the space hollow and intersected with the crystals previously formed.

On the Composition of Wolfram.

By J. Persoz.[*]

When crude tungstic acid, in the state in which it is obtained from wolfram, is fused with five or six times its weight of nitre, at a gradually increasing temperature, three distinct salts are obtained, possessing different characters, and derived from essentially different acids.

* Compt. Rend. XXXIV, 135.

If the heat be raised only a little above the melting-point of the nitre, part only of the crude tungstic acid is attacked ; and, on treating the product with hot water, we obtain a solution of a salt *A*, and an insoluble residue *x*.

The residue *x*, treated with a large excess of nitric acid at a temperature a little below that at which the nitre decomposes, becomes very fluid, but not transparent.   On treating the product with boiling water, the excess of nitre is dissolved, together with a large quantity of another salt *B*, and there remains an insoluble salt *C*, which passes through the filter as soon as the wash-water becomes pure.

The solution *A*, when left to itself, first deposits free nitre, if any of that substance be present, and afterwards agglomerates into a mass of crystals, composed of nitre and water, together with a very small quantity of a salt belonging to the tungstic group.   Boiling water decomposes these crystals, dissolving the nitre, and leaving a flocculent residue, which, when digested and frequently washed with hydrochloric acid, is converted into a *mealy powder*, very soluble in water, but insoluble in those acids which have a great attraction for water.   The solution, when evaporated to dryness, leaves a yellowish-white residue, which, if unaccompanied by foreign matter, redissolves completely in water, forming a solution possessing strongly acid characters.   This solution is not precipitated by nitrate of silver; zinc reduces it, forming the blue oxide.   When treated with acids which have a strong attraction for water, it loses its water of hydration, and reproduces the mealy powder above mentioned.   When evaporated in vacuo, it leaves a yellow crystalline mass, which, if the acid is very pure, is composed of regular octohedrons.

Salt B.—This salt is composed of excess of nitre, mixed with tungstate of potash, properly so called.

Insoluble salt C.—When this salt is heated to redness with caustic potash, and the fused mass digested in water, a residue of oxide of iron is obtained, together with a solution, which, when treated with a slight excess of nitric acid, forms, on boiling, a milk-white, pulverulent precipitate, which is likewise an acid distinct from either of the preceding.   This acid and all its salts exhibit the peculiar property of passing through the filter when washed with pure water. It resembles ordinary tungstic acid in most of its properties; but differs from it by certain very decided characters; for example, it changes from white to yellow when heated, and recovers its original colour on cooling.   In other characters it seems to bear some resemblance to niobic acid.

VII.—*On a New Method of obtaining Hippuric Acid in considerable quantity without evaporation of the Urine; and on some of its Products of Decomposition.*

BY EDWARD RILEY, F.C.S.,

ASSISTANT AT THE MUSEUM OF PRACTICAL GEOLOGY.

The preparation of hippuric acid by the methods usually adopted is tedious, and involves considerable labour. Many processes have been proposed, but all experimenters on this subject have adopted the plan of evaporating the urine to $\frac{1}{6}$ or $\frac{1}{8}$ of its original bulk. H. Schwarz mentions,* in speaking of the preparation of hippuric acid, that a urine is rarely obtained which gives hippuric acid simply on the addition of hydrochloric acid, without evaporation. Löwig also mentions, that by the addition of hydrochloric acid to cow's urine, a crystalline precipitate is deposited, which the older chemists considered to be benzoic acid.

I shall now describe some experiments by which I have been led to a simplification of the method of preparing this acid. Three parts of fresh cow's urine obtained from the same cow were treated according to Liebig's process, as given in Turner's "Elements of Chemistry;" the cow from which it was voided was fed upon brewers' grains twice in the twenty-four hours, and allowed to graze on a neighbouring common. The urine was heated on a water-bath from a half to three-quarters of an hour with an excess of milk of lime, during which time distinct traces of ammonia were evolved; it was then filtered from the undissolved lime, neutralized

* Chem. Gaz. Aug. 1, 1845.

with hydrochloric acid, left slightly acid, and then evaporated to about $\frac{1}{8}$ or $\frac{1}{10}$ of its original bulk; the portion that crystallised on cooling was filtered from the residue, and purified by treating it three times with animal charcoal and lime, and then crystallising. Thus obtained, it was perfectly white, and in long acicular needles; but the quantity did not amount to more than from 5 to 10 grains.

The quantity being small, three other pints of urine were treated as above described, except that, after filtration the lime was left in excess; the evaporation was not so rapid as in the former case. From the small solubility of hippuric acid, I thought some might be obtained, although it was only evaporated to $\frac{1}{4}$ of its original bulk. Hydrochloric acid was added, an immediate precipitate was formed which appeared in exceedingly minute crystals, almost like an amorphous powder; this was filtered off. Thinking that more might possibly be procured, another portion of acid was added: a very considerable quantity, amounting to five or six times that previously obtained, was deposited, and removed by filtration. This unexpected result induced me to add another portion of acid, and as large a quantity was produced as in the second case; this was separated from the liquid, which now ceased to give any further precipitate on the addition of an acid. From these circumstances, it was obvious that hippuric acid must be more insoluble in a very acid solution in the cold, than in a solution slightly acidulated.

Hydrochloric acid was added to some of the urine that had not been used in the previous operation, and in a few seconds, crystals began to form, shooting out in needles from a nucleus; after it had stood a few minutes, the bottom of the flask was completely covered with a crystalline deposit of hippuric acid of considerable thickness. The amount of hippuric acid obtained from the three pints concentrated by evaporation, amounted to about 6 oz. by measure after the liquid had been decanted. These results led to some further experiments on the urine of cows. The urine from several cows was tested at various times, and generally gave large quantities of hippuric acid on addition of hydrochloric acid.

It was found from various experiments, that $\frac{1}{2}$ oz. of hydrochloric acid to a pint of urine, gave the best results. Sulphuric acid appeared to separate colouring matter.

Sometimes but little was to be obtained from the urine, at other times very considerable quantities were obtained. The urine was tested in the following manner: about 3 or 4 oz. of it were poured into a precipitating glass with about $\frac{1}{2}$ to $\frac{3}{4}$ of a drachm of hydrochloric acid. If no precipitate appeared it was vigorously

stirred, when hippuric acid would be precipitated in considerable quantity at the bottom of the glass. If, on the contrary, the liquid were not stirred, needle crystals would shoot out from a nucleus, some adhering to the sides of the glass, others falling to the bottom.

It was desirable to know the exact quantity of hippuric acid that could be procured: 1 pint of urine was taken from a cow, ½ oz. by measure of commercial hydrochloric acid added; it was then allowed to stand twelve hours, filtered on two filters, one exactly counterpoising and encircling the other, and dried gradually in the air, until it ceased to lose weight. The weight thus obtained was

<div align="center">158·83 grains,</div>

calculated per cent gives   2·269
    ,,   per imp. gal.   1270·64   or 2·9 oz. avoirdupoise.

The hippuric acid was only slightly coloured. It was lightly scraped from the filter, and the filters were again weighed, when the excess was found to be 0·92.

This deducted, and calculated as before, gives 157·78 grains,

calculated per cent gives .   2·252
    ,,   per imp. gal.   1262·240 or 2·88 oz. avoirdupoise.

Thus showing, that the little colouring matter on the filter made no appreciable difference, in fact, some small quantity of hippuric acid was left adhering to it.

The method of obtaining and purifying the hippuric acid was as follows : the urine was caught from five to seven in the morning from seven cows, the urine from each being put into a separate vessel; each urine was tested in the manner before described; that which gave an immediate precipitate on stirring, was poured into a large vessel, whilst the rest was rejected. It was mixed with commercial hydrochloric acid in the proportion of ½ oz. by measure to a pint; this was left until the evening, when the hippuric acid was decanted from the supernatant liquor, and was afterwards thrown on a square filter; the urine collected during the day, was then treated in a similar manner, and filtered off the following morning. I have in this way, obtained from a gallon, as much as would twice fill a small 2 oz. ladle when pressed down tight, and sometimes rather more; the hippuric acid was freed from the excess of urine, by twisting it in a piece of linen into a ball, and then squeezing it until no more liquid was expressed.

When about seven of these measures had been obtained, amounting

<div align="center">H 2</div>

to 1½ lb. by weight, of the moist hippuric acid, all the urine being expressed that was possible by simple pressure, it was placed in a large thin milk-pan, of a capacity of 2½ gallons, rain-water added, and an excess of lime, and about 3 oz. of commercial animal charcoal ; the milk-pan was then placed over an ordinary washing-copper, and the water in the latter heated to boiling. The mixture was heated until all the hippuric acid was dissolved, then kept at the same temperature about half an hour longer, filtered through large filters into another similar pan, replaced on the copper, heated until the temperature did not rise, then neutralized with hydrochloric acid, and about 4 to 5 oz. by measure more of the hydrochloric acid added. It was carefully covered and left until the next morning, when the liquid was found to be still luke-warm ; but magnificent crystals, of the square prismatic form, sometimes 2 inches in length, were found adhering to the sides and bottom of the dish ; the dish was allowed to cool on the copper, which was not cool on the evening following that on which it was purified.   The crystals were drained, and allowed to dry between blotting-paper. The crystals thus obtained had only a slight tinge of colour, being sometimes rather more, some-times rather less than ½ lb. in weight.   I have occasionally obtained them nearly white, by the first crystallization, when the animal charcoal was good. By repeating the above operation on the crys-tals, they may be obtained in beautiful snow-white prisms, without a tinge of colour. It often happens that the whole of the hippuric acid does not crystallize out, that sometimes considerable quantities may be obtained by adding 4 or 5 oz. of hydrochloric acid to the mother-liquor ; a small portion of the mother-liquor should always be tested, to see whether any more acid may be obtained from it ; this sometimes happens in purifying the acid at one time, whilst not at another.

The acid prepared in the above manner was submitted to analysis, after being twice recrystallized from distilled water, to purify it from a trace of lime which it invariably contains; when prepared as above, it gave, on analysis, results agreeing with the established formula :
$C_{18} NH_8 O_5 + HO.$

It is important to know from what food the greatest quantity of hippuric acid is produced. The observations made on this subject tend to show, that when cows are fed on grass, the hippuric acid exists in the urine in the largest quantity. The urine from cattle fed on other food does not give so large a quantity of hippuric acid.

I think we may infer (though perhaps not without a doubt), that the hippuric acid is obtained from the grasses in the pastures, some

of which contain a peculiar substance, cumarin, thought to be benzoic acid previously to the examination of Dr. Bleibtreu,* which probably may, by its passage through the animal organism, be transformed into hippuric acid, the cumarin occurring in the *Anthoranthum odoratum*, or spring grass, common in our meadows; also in the *Melilotus officinalis*, or melilot, and in the *Asperula adorata*, or woodruff. This subject I hope to investigate.

Through the kindness of Professor Miller, of Cambridge, I am enabled to give the form of the crystals of hippuric acid, which, previously to his examination, I thought I had succeeded in obtaining in two different forms; but he assures me they are similar.

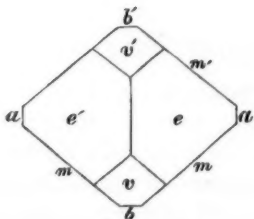Prismatic symbols of the simple forms:

a 100, b 010, c 001, e 101, v 011, m 110, r 111.

The face c is common to the zones $e\,e'$, $v\,v'$; c is common to the zones eb, va.

The faces a, b, c, r, are very small.

The angles between normals to the faces are:

$b\,c$	90°	0′
$c\,a$	90	0
$a\,b$	90	0
$v\,v'$	91	35
$e\,e'$	81	32
$m\,m'$	79	58
$e\,m'$	65	11
$v\,e$	58	7
$v\,m'$	56	42
$r\,v$	31	1
$r\,m$	36	41

Cleavage c, tolerably perfect.

Strong acids, as is well known, decompose the hippuric acid into benzoic acid and glycocol. Dilute nitric acid may be used to purify hippuric acid, the nitric acid only destroying the colouring matter. I have in this way obtained very good crystals, free from colour. Strong hydrochloric acid readily dissolves hippuric acid; and after boiling some time, the mass becomes turbid, and an oily substance of a dark colour floats on the surface, viz., benzoic acid, which crystallizes on cooling, and may be separated by filtration from the hydrochlorate of glycocol, which remains in solution.

The benzoic acid thus obtained, being submitted to sublimation in

* Mem. Chem. Soc. III, 205.

the apparatus described by Mohr, gives beautiful crystals of perfectly white benzoic acid, with only a slight odour.

I have obtained considerable quantities of benzoic acid by the above method, and am convinced that it might be prepared from this source much more economically than from gum benzoin.

I have also prepared glycocol from the mother-liquor by the method of Dessaignes. In reference to this substance, I may mention that I have not been able to obtain the fiery-red colour mentioned by Mr. Horsford, on heating glycocol with a strong solution of potash. Schwarz* makes the same observation.

I have prepared glycocol by the action of sulphuric acid on hippuric acid, which appears to act as well as hydrochloric acid. The excess of sulphuric acid is removed, and the sulphate of glycocol decomposed by precipitated carbonate and a little hydrate of baryta, whereby a sweet solution is obtained which crystallizes in apparently different crystals to those prepared by the action of hydrochloric acid on hippuric acid; they all effloresce on exposure to the air. They have not been analyzed.

VIII.—*Contributions towards the history of Tannic Acid.*

By Dr. Strecker.

(FROM A LETTER TO DR. HOFMANN.)

The opinions of chemists regarding the transformation of tannic into gallic acid are still divided. Whilst some assume that tannic acid splits into gallic acid, carbonic acid and water, Mulder has lately asserted that the whole amount of carbon in tannic acid passes over into gallic acid, only water being assimilated, so that the two acids would contain the same number of carbon equivalents; and Wetherill has even gone so far as to consider tannic and gallic acids as isomeric.

The observation that the distillation of tannic acid, even when conducted with the utmost care, invariably yields a certain amount of a non-volatile residue, whilst, according to the old formula, it should split exactly into pyrogallic acid, carbonic acid and water, together with the well-known fact that the action of powerful acids upon tannic acid invariably gives rise to the formation of an ulminlike body, whilst gallic acid is not affected by acids of the same

* Chem. Gaz. 1850, 475.

concentration, suggested to me the idea that tannic acid might contain another compound in addition to gallic acid.

On examining the question, I have arrived at the curious result that tannic acid, when acted upon by acids, yields, together with gallic acid, *sugar*, so that henceforth tannic acid may be classed with the conjugate sugar-compounds. I have thrown down a solution of pure tannic acid with sulphuric acid; boiled the precipitate of sulphate of tannin with water, or very dilute sulphuric acid; neutralised the solution with carbonate of lead; and precipitated the gallic acid still dissolved with acetate of lead. The liquid, when freed from the excess of acetate of lead by hydrosulphuric acid, gave, on evaporation, a syrupy residue, possessing all the properties of sugar, modified by acids. It reduced an alkaline solution of protoxide of copper, although it did not contain a trace of gallic acid (which produces the same effect), and readily fermented on addition of yeast. This latter experiment appears to me conclusive. Accordingly, the formula of tannic acid will have to be altered; and although I have not yet been able to determine the quantity of sugar which is produced by a known weight of tannic acid, I nevertheless even now believe that the composition of this substance is represented by the formula:

$$C_{40} H_{18} O_{26},$$

as will be seen from the subjoined comparison of the numbers found and calculated:

		Theory.	Berzelius.	Liebig.	Mulder.		Strecker.	
C_{40}	. .	51·5	51·5	51·5	51·5—52·1		51·4—51·5	
H_{18}	. .	3·8	3·8	4·1	3·6— 3·9		3·9— 3·9	
O_{26}	. .	44·7	—	—	—	—	—	—
		100·0						

Thus the transformation would take place according to the following equation:

$$C_{40}H_{18}O_{26} + 10 \, HO = 2 \, (C_{14}H_8O_{12}) + C_{12}H_{12}O_{12}.$$
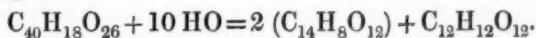
As the number of water-equivalents which is assimilated in this change is unusually large, the question arises whether tannic acid is a perfect analogue of the other conjugated sugar-compounds; at all events, we have to assume a hydrate of carbon in a state of conjugation.

From these experiments it is evident that this conjugate sugar-compound belongs to the principles most universally diffused in vegetable nature, and it can scarcely be doubted that the other tannin-like substances will have an analogous composition.

IX.—*On the detection and qualitative separation of Tin, Anti-*
mony, and Arsenic; and on the relation existing between these
metals, and others which are precipitated from their acid solutions
by Sulphuretted Hydrogen.

By Charles L. Bloxam.

The difficulty which I experienced, some years since, in the analysis
of the alloy known as Britannia Metal, from the want of a certain
and ready method of separating tin, antimony, and arsenic, induced
me to undertake a close investigation into the reactions of these three
metals; and the results of this inquiry have appeared to me to possess
so much interest, that I venture to lay them before the Society.

There is, perhaps, no problem in the whole range of qualitative
analysis which has engaged so much attention, and so repeatedly
defied all attempts at solution, as the separation of the three metals
under consideration; and the reason of this is, evidently, the great
similarity in properties exhibited by two of the metals, antimony and
arsenic, conjoined with the disposition of the third, tin, to form an
insoluble binoxide, which enters into combinations, likewise insoluble,
with the oxides of antimony and arsenic.

Before describing the method which I have found the most effective
for the separation of these metals, I shall briefly pass in review some
of those which have been already proposed for effecting this object.
In doing this, however, I shall only mention those methods which
are applicable in ordinary qualitative analysis, omitting those which
were designed only for the separation of the metals in particular
cases, as well as those processes which require a great expenditure,
either of time or skill, on the part of the analyst.

The observation made some years ago by Levol,* that the three
metals could not be separated by means of nitric acid, perfectly
coincides with the result of my own experiments, which have shown
that small quantities of arsenic are not dissolved out of a mixture
containing tin, antimony, and arsenic, by nitric acid.

The method proposed by Simon† for the detection of small
quantities of arsenic in the presence of antimony, consists in fusing
the mixed sulphides of these metals with nitrate of potash, extracting
the fused mass with water, acidulating the filtered solution with nitric

* Ann. Chim. Phys. [3] XVI, 493.
† Pogg. Ann. XL, 411.

acid, adding nitrate of silver, and precipitating the arseniate of silver by the careful addition of ammonia.

In order to ascertain whether this method could be applied to the separation of the three metals in cases where but a small quantity of arsenic is present, I prepared a solution containing

<div align="center">

0·0475 grm. antimony,

0·0475　,,　tin,

and　　0·0050　,,　arsenic,

</div>

(corresponding to 47·5 per cent of antimony, 47·5 per cent of tin, and 5 per cent of arsenic,) but failed in detecting the arsenic by treating the precipitated sulphides according to the method detailed above. I have found, moreover, as would be expected, that this method is very unsafe, even for the detection of larger quantities of arsenic; since it is very difficult to add exactly the amount of ammonia necessary to neutralize the free acid, and it is well known that the arseniate of silver is soluble in the slightest excess, either of nitric acid or of ammonia.

I have also tried to apply to the separation of antimony, tin, and arsenic, the method recommended by Meyer* for the separation of antimony and arsenic. This method consists in fusing the mixed metals (antimony and arsenic) or their sulphides, oxidised by nitric acid, with nitrate of soda, and extracting the arseniate of soda from the fused mass with water, which leaves the antimony in the residue. Since, if tin were present, it would also be left in the residue, I thought it might be practicable to separate the antimony and tin by treating this residue with tartaric acid. Bisulphide of tin was dried and fused with nitrate of soda; the fused mass was extracted with cold water; the aqueous solution was perfectly free from tin; the residue was washed, and boiled with a concentrated solution of tartaric acid, the solution filtered, mixed with hydrochloric acid, and subjected to a current of sulphuretted hydrogen, when a yellow precipitate of bisulphide of tin was obtained.

Moreover, when tersulphide of antimony was treated according to this process, the residue left by water could not be entirely dissolved by tartaric acid.

These experiments proved that no dependence could be placed upon this method for the separation of antimony and tin.

Some experiments have also been tried upon the method recently proposed by Fleitmann† for the detection of tin, antimony, and arsenic.

* Ann. Ch. Pharm. LXVI, 236.

† Ann. Ch. Pharm. Jan. 1851.

This method consists in testing for arsenic in one portion of the solution, by adding excess of potassa, and boiling with metallic zinc, when, if arsenic be present, arsenietted hydrogen will be evolved, and may be recognised by its property of blackening a solution of nitrate of silver; whilst antimony and tin are detected by treating the other portion of the solution with zinc and hydrochloric acid, and kindling the hydrogen which is evolved; the flame of antimonietted hydrogen is known by its depositing, upon a porcelain plate, a spot of antimony, insoluble in solution of hypochlorite of soda, whilst the arsenic spot is soluble in this reagent. The tin is then detected by boiling the metals reduced by zinc, with hydrochloric acid, and testing the solution for protochloride of tin with hydrosulphuric acid.

In order to prove this method, I employed it in testing a solution containing

<div style="text-align:center">

0·095 grm. tin

and　　　　0·005 　„　antimony,

</div>

when the metallic stain, deposited upon a porcelain dish, was not redissolved by solution of chloride of soda (prepared by transmitting a very slow current of chlorine through a dilute solution of carbonate of soda, until it was but slightly alkaline).

On the other hand, when a solution containing

<div style="text-align:center">

0·095 grm. tin

and　　　　0·005 　„　arsenic

</div>

was employed, the metallic stain was instantly dissolved by solution of chloride of soda.

I could not succeed in detecting the antimony by this method in solutions containing respectively :

<div style="text-align:center">

0·099 grm. arsenic

and　　　　0·001 　„　antimony,

0·495 grm. arsenic

and　　　　0·005 　„　antimony,

and

0·095 grm. arsenic

and　　　　0·005 　„　antimony,

</div>

since, in these three cases, the very large metallic crusts which were deposited upon the porcelain, dissolved entirely in solution of chloride of soda.

Hence it appears, that this method does not enable us to detect even 5 per cent of antimony in a mixture of that metal with arsenic.

The test for arsenic furnishes results which are far more satisfactory.

A solution containing

$$0.095 \text{ grm. tin}$$
$$\text{and} \qquad 0.005 \text{ ,, arsenic}$$

was mixed with a considerable excess of potash, and a few fragments of granulated zinc (free from arsenic) introduced; the flask containing the mixture was then fitted with a perforated cork carrying a short piece of wide glass tube, and heated to boiling upon a sand-bath; when a piece of paper spotted with solution of nitrate of silver was held over the extremity of the tube, the black arsenide of silver was immediately formed.

In another experiment, a solution containing

$$0.495 \text{ grm. antimony}$$
$$\text{and} \qquad 0.495 \text{ ,, tin}$$

was treated according to the above method; no black spot was visible upon the paper, but when 0.01 grm. arsenic was added to the mixture, a black spot was at once produced.

Other experiments were tried, all tending to show that this test is a most valuable one for arsenic in the presence of antimony, and will probably be found of great service in judicial investigations, especially as it may, in all probability, be applied equally well to a potash solution of the sulphides of these metals.

The objections which seem to me, therefore, to restrict the application of Fleitmann's method, have regard chiefly to the test for antimony, since it has been shown that small quantities of this metal may escape detection; moreover, the solution of chloride of soda cannot be preserved for any length of time, and the operation requires a special apparatus, which it is well, if possible, to avoid in qualitative analysis.

I have attempted to apply, qualitatively, the last method proposed by Rose* for the quantitative separation of tin, antimony, and arsenic, which consists in fusing the mixed oxides (obtained by treating the metals with nitric acid) with caustic soda, digesting the fused mass with water, and precipitating the last traces of antimoniate of soda by means of alcohol.

Tersulphide of antimony was oxidised with nitric acid, dried, and fused with a large excess of hydrate of soda in a silver crucible; the fused mass was digested with cold water, and set aside for twelve

* Berl. Monatber.; Pogg. Ann. LXXIII, 582.

hours; the solution was then filtered, and mixed with somewhat more than one-third of its volume of strong alcohol, and allowed to stand during the night; a considerable quantity of antimoniate of soda was deposited, and, on filtering this off, and testing the clear liquid with hydrochloric and hydrosulphuric acids, scarcely a trace of antimony was detected.

When tersulphide of arsenic was treated in exactly the same manner, and the aqueous solution of the fused mass was mixed with alcohol and allowed to stand for some hours, numerous small crystals were deposited, which, after washing with alcohol till free from adhering arsenic, were shown to contain this metal in considerable quantity; this circumstance, of course, would prevent the application of the method in qualitative analysis, since it appears that unless attention be paid to the strength and quantity of the spirit, as mentioned in Rose's paper, arsenic and antimony might both be found in the precipitate; moreover, I may cite, as an objection to the qualitative application of this process, the rather considerable quantity of substance required, which is seldom at our disposal in the examination of this group of oxides.

I have also found that a small quantity of arsenic cannot be detected in a mixture of the three metals, by this method of fusion with hydrate of soda.

An alloy containing a large quantity of tin, together with small quantities of antimony and arsenic, was oxidised with nitric acid, and the residue fused with excess of hydrate of soda; the fused mass was boiled with water, in which it almost entirely dissolved; the solution was acidulated with nitric acid, and filtered; the filtrate was carefully tested for arsenic by evaporating to a small bulk, mixing with excess of ammonia, evaporating to dryness, redissolving in water, and adding nitrate of silver, when no precipitate whatever was obtained; on the other hand, the precipitate produced by nitric acid in the aqueous solution of the fused mass, was mixed with charcoal, and reduced with cyanide of potassium and carbonate of soda in a crucible; the metallic button was found to contain arsenic.

Rose's method is also inapplicable in ordinary qualitative analysis to the separation of antimony and tin, because, previously to oxidation by nitric acid, these must be reduced to the metallic state, which cannot be conveniently effected when small quantities are to be examined.

The following experiment was made to ascertain whether the residue obtained by oxidising the tersulphide of antimony with nitric

acid would behave in the same way, when fused with hydrate of soda, as that produced by the oxidation of the metal.

Tersulphide of antimony was oxidised with nitric acid, dried and fused with a large excess of hydrate of soda; the fused mass was digested with cold water, and allowed to stand for twelve hours; the aqueous solution was filtered, acidulated with hydrochloric acid, and sulphuretted hydrogen passed; a considerable quantity of orange sulphide of antimony was precipitated.

When bisulphide of tin was oxidised with concentrated nitric acid, dried, fused for a considerable time with a large excess of hydrate of soda, and the fused mass digested for twenty-four hours with cold water, it slowly dissolved, leaving a very slight residue, which was filtered off, but passed through the filter when I attempted to wash it; a repetition of the experiment gave a similar result; this would point out a serious difficulty, since it would be highly important that the fused mass should form a perfectly clear solution, if no antimony were present.

An experiment has been tried upon the method of separation recommended in Galloway's manual of qualitative analysis.

Bisulphide of tin was gradually added to fused nitrate of ammonia, and the mixture heated for some time, until all nitrate of ammonia had volatilised, and finally, strongly ignited for some minutes.   The ignited residue was boiled with a strong solution of tartaric acid, filtered, the solution mixed with hydrochloric acid, and sulphuretted hydrogen passed; a decided, though it must be confessed not very abundant, yellow precipitate was obtained.   I had previously often observed the partial solubility of the binoxide of tin in tartaric acid, which may deceive us as to the presence of antimony.

The method of Levol* for the separation of tin and antimony, which consists in boiling the finely-divided metals with hydrochloric acid, is inapplicable in ordinary analysis, because, unless the precautions pointed out by the author of this method be strictly adhered to, part of the antimony is dissolved by hydrochloric acid, as was originally shown by Elsner,† whose results have been confirmed by my own observations.

I have also tried some experiments upon the old method of separating tin and antimony by boiling the metals reduced by zinc, with nitric acid, and separating the mixed oxides thus obtained, by means of tartaric acid or bitartrate of potash.

Antimony which had been precipitated by zinc from a solution of

* Ann. Ch. Phys. XIII, 125.
† J. Pr. Chem. XXXV, 313.

the terchloride, was oxidised by heating with a mixture of concentrated nitric acid with two volumes of water; the oxide was well washed, and boiled with a saturated solution of tartaric acid for some hours; it would not entirely dissolve; the oxide prepared by using more dilute nitric acid dissolved to a somewhat greater extent. Bitartrate of potash was also tried with the same result.

Marsh's method of separating tin and arsenic, which consists in the evolution of the latter as arsenietted hydrogen by digesting the acid solution with zinc, is not applicable in ordinary analysis; firstly, because of the difficulty of obtaining, in every case, a solution free from nitric acid; secondly, because tin is sometimes an impurity of commercial zinc, and thirdly, because antimony interferes with the detection of the arsenic.

The process of Fresenius and Babo,* in which the arsenic is reduced by cyanide of potassium and carbonate of soda, in a stream of dry carbonic acid, is unexceptionable as far as the detection of arsenic is concerned; neither antimony nor tin interferes with this test; I have repeatedly tested pure sulphide of antimony by this method, without obtaining any trace of metallic sublimate. Unfortunately, however, so small is the quantity of the mixed sulphides that can be employed in this operation, that it is hopeless for an ordinary analyst to attempt the separation of antimony and tin in the residue.

After having satisfied myself that no certain and easy method existed of separating antimony, tin, and arsenic, I tried a great number of experiments with the view of discovering such a method; and since, in the course of these attempts, I have met with some reactions of these metals of which I nowhere find any account, I may perhaps be permitted to bring forward a few of them, as it appears to me a by no means unimportant branch of analytical science, to know what methods will not be competent to effect a particular separation.

Tersulphide of antimony was fused with Liebig's cyanide of potassium, with continual stirring; the mass was retained in fusion for some time; while fused, it had a deep brown colour, but became white on cooling; the mass dissolved entirely in water, and the solution gave an orange precipitate on addition of dilute hydrochloric acid; I was astonished, that in this experiment, no reduction of the antimony had taken place.

When bisulphide of tin was treated in a similar manner, globules of metal were obtained, and acetic acid, added to the aqueous solution, gave a yellow precipitate.

* Ann. Ch. Pharm. XLIX, 287.

When either bisulphide of tin or tersulphide of antimony was fused with nitrate of soda, and the mass extracted with cold water, neither metal was found in solution, but the residue left by water was, in each case, partly soluble in tartaric acid.

Tersulphide of antimony was added to fused chlorate of potash; the fused mass powdered, and boiled with water; much antimony was found in the aqueous solution; but when bisulphide of tin was thus treated, no tin whatever was found in the solution; when a mixture of bisulphide of tin with a little tersulphide of antimony was employed, all the antimony was left behind in the residue.

Tersulphide of antimony was fused with nitrate of potash, the mass powdered, and digested with cold water; the solution contained no antimony, and the residue was only partly soluble in hydrochloric acid.

Bisulphide of tin behaved in a similar manner.

When freshly precipitated tersulphide of antimony was oxidised with cold or hot concentrated nitric acid, a portion of antimony was found in the solution, and the residue was almost entirely dissolved when boiled with solution of tartaric acid. The nitric solution contained more antimony when a mixture of one volume of the concentrated acid with two volumes of water was employed. The tersulphide of antimony dissolved almost entirely, in a mixture of the concentrated nitric acid with four volumes of water.

On boiling bisulphide of tin with very dilute nitric acid, no tin was found in the solution.

A solution of terchloride of antimony was boiled with excess of carbonate of lime, and filtered; antimony was still found in considerable quantity in the solution.

When a solution of bichloride of tin was treated in the same manner, no tin was found in solution.

However, when a solution containing a large proportion of tin and a small quantity of antimony was neutralised with carbonate of lime and filtered, no antimony was found in solution; the same result was obtained on boiling.

In the course of my examination into the reactions of antimony and tin, I found that when a solution of terchloride of antimony was mixed with an excess of solution of sesquicarbonate of ammonia, and boiled, the precipitate at first produced was entirely redissolved; whilst, on making the same experiment with solution of bichloride of tin, no tin whatever was found in the filtered solution.

Thinking that this observation might lead me to the separation of these metals, I examined the reaction more minutely, and invariably

found that no tin could be detected in solution after boiling with an excess of sesquicarbonate of ammonia. I discovered, however, that occasionally this reagent produced, in a solution, of terchloride of antimony, a precipitate which was not perfectly soluble in excess, although a large quantity of antimony was invariably found in the solution. Finding that this precipitate was always less after boiling the terchloride of antimony with a little nitric acid, I tried whether the treatment of the solution with powerful oxidising agents would ensure the complete solubility of the precipitate. With this view, I tried successively, chlorine, chloride of soda, and chlorate of potash, in the presence of free hydrochloric and nitric acids, but always with the same result, namely, that although in many cases the precipitate was entirely soluble in excess, it depended so much upon the strength of the solution and upon the amount of sesquicarbonate of ammonia added, that it would be in vain to attempt or expect the complete solution of the antimony, although it was invariably found that the tin was entirely precipitated. I therefore determined to have recourse to a special method for the detection of tin in the precipitate. After several trials, I found that the best special reaction for this metal was that of the hydrochloric solution with protochloride of mercury, by which an incredibly small amount of tin may be detected. The precipitate produced by sesquicarbonate of ammonia was fused with cyanide of potassium, the fused mass digested with water, and the reduced metal boiled with hydrochloric acid; the filtered hydrochloric solution was then tested with protochloride of mercury, when, if a very small quantity of tin was present, it gave a very highly crystalline precipitate; with a larger quantity, a precipitate not visibly crystalline; and when very much tin was present, a grey precipitate of metallic mercury.

In order to ascertain to what extent the above method was applicable to the separation of antimony and tin in the ordinary course of analysis, I analysed solutions containing weighed quantities of these metals, always proceeding according to the following routine.

The solution containing the two metals was precipitated by sulphuretted hydrogen; the sulphides washed upon a filter, dissolved in yellow sulphide of ammonium, reprecipitated by hydrochloric acid, with addition of a little hydrosulphuric acid; the precipitate, after washing, dissolved in hydrochloric acid with a little nitric acid; the solution mixed with an excess of sesquicarbonate of ammonia, boiled for a few minutes, filtered; and the filtered solution, after concentration, tested for antimony, by acidulating with hydrochloric acid and passing sulphuretted hydrogen.

The filter, with the white precipitate produced by sesquicarbonate of ammonia, after washing twice or thrice with this reagent (for, when washed with water, it passes through the filter), was dried, incinerated in a porcelain crucible, the ash fused with a little cyanide of potassium, and treated as above described, in order to detect the tin.

By this process I have succeeded perfectly in detecting the two metals, even in cases where they have been mixed in the proportions of 99 to 1, and when only 0·003 grm., or even less, of the metal which was in small quantity, has been present. In these cases, the tin was always present in the form of bichloride, and the antimony either as terchloride or pentachloride.

I may mention, as an important precaution when testing for traces of tin, that the reduced metal should not be boiled for any considerable period with hydrochloric acid, since I have found that the reaction with protochloride of mercury cannot then be obtained; whereas, it is quite sufficient to raise the acid to the boiling-point, when the merest trace of tin may be detected.

In the course of these experiments, I have also found that the pure canary-yellow colour of the bisulphide of tin may be altered, in a very remarkable manner, by the presence even of very small quantities of antimony; in fact, most ordinary solutions of bichloride of tin were found to give a greenish-yellow precipitate from this cause, and a very slight admixture of antimony in a solution of tin could be detected in this manner.

A solution containing

> 99·95 parts of tin, as bichloride,
> and   00·05   ,,   antimony, as terchloride,

gave, with sulphuretted hydrogen, a precipitate which had a decided green tinge when compared with pure bisulphide of tin.

With a solution of

> 99·45 tin
> and   00·55 antimony,

the precipitate had a distinct green colour; and on increasing the proportion of antimony, it became very dark. I thought at first that the dark colour might be due to the presence of protochloride of tin, but could not detect any in the solution.

Having satisfied myself of the accuracy of the above process for the detection of the tin and antimony, I next inquired how far the presence of arsenic would interfere with it. I found that when

arsenic was present, the addition of sesquicarbonate of ammonia failed to throw down the whole of the tin; and in a case where the latter amounted to 5 per cent of the arsenic, no precipitate whatever was produced by sesquicarbonate of ammonia; moreover, the presence of arsenic of course interfered with the subsequent detection of the antimony in the filtrate from the binoxide of tin. It therefore became necessary to find some method of separating the arsenic from the antimony and tin, before taking any steps to separate these metals from each other.

Finding that, as I have already stated, all the tin was precipitated from a solution of the bichloride by carbonate of lime, even in presence of chloride of ammonium, and that arsenic acid appeared not to be precipitated at all under the same circumstances, I attempted to detect by this method, 1 part of arsenic, as arsenic acid, in the presence of 20 parts of tin in the form of bichloride, but found that the whole of the arsenic was carried down with the binoxide of tin.

I also tried to separate them by oxidising the sulphides with nitric acid, and fusing the residue with cyanide of potassium at a high temperature, but found that arsenic could not be entirely expelled in this way.

When a mixture of bisulphide of tin and tersulphide of arsenic (containing 1 part of tin to 20 parts of arsenic) was oxidised with nitric acid, the residue dried, ignited; and boiled with water until the aqueous solution gave no further indication of arsenic, this metal could still be detected in the residue.

It was found that when the residue obtained by oxidising a mixture of bisulphide of tin and tersulphide of arsenic (containing equal weights of these metals) with nitric acid, was fused with hydrate of soda; the fused mass dissolved in water; an excess of nitric acid added; the solution evaporated to dryness; and the residue boiled with water; the merest trace of arsenic was found in the solution.

This experiment was repeated with the same result.

A mixture of bisulphide of tin and tersulphide of arsenic containing equal weights of these metals, was fused with nitrate of potash; the fused mass dissolved almost entirely in water, and the aqueous solution, when acidulated with nitric acid, and heated, gave an abundant precipitate, which, after thorough washing, was found to contain arsenic.

Having failed in these attempts to discover a method for the complete separation of arsenic, I had recourse to the extraction of the sulphides of arsenic from a mixture of these with the sulphides of

tin and antimony, by means of sesquicarbonate of ammonia, a method which has been occasionally employed by other analysts.

I found that when pure tersulphide or pentasulphide of antimony was digested, either with or without heating, in a solution of sesquicarbonate of ammonia (prepared by agitating the commercial salt with cold water as long as any was dissolved), very small quantities of the sulphides were taken up, so small indeed, that this degree of solubility did not appear likely to interfere in analysis, whilst the two sulphides of arsenic dissolved at once in this reagent.

When bisulphide of tin was treated in the same manner, none was dissolved, even on boiling with sesquicarbonate of ammonia.

To ascertain how far the solubility of the sulphides of antimony would affect the result if sesquicarbonate of ammonia were used, I precipitated, by sulphuretted hydrogen, a solution containing bichloride of tin and terchloride of antimony, in the proportions of 99 parts of tin to 1 part of antimony, dissolved the precipitated sulphides in yellow sulphide of ammonium, reprecipitated by hydrochloric acid, and digested the precipitate with a saturated solution of sesquicarbonate of ammonia. I found that, although a little antimony was contained in the solution, the greater part remained in the residue, and the same result was obtained in several experiments.

The next question to be decided was, how far the behaviour of the sulphides of arsenic with sesquicarbonate of ammonia would be modified by the presence of those of antimony and tin.

Sulphuretted hydrogen was passed through a solution containing arsenic and antimony in the proportion of 99 : 1 (about 0·004 grm. of antimony being present), the arsenic as arsenious acid dissolved in hydrochloric acid, and the antimony as terchloride. The precipitate thus obtained was washed, and digested in a saturated solution of sesquicarbonate of ammonia, with the aid of a gentle heat; a fine orange-yellow residue of tersulphide of antimony was left undissolved. This experiment was repeated many times with the same result.

When the proportion between the two metals was reversed, there being about 0·0035 grm. of arsenic present, the latter was detected with great ease in the solution of the sulphides in sesquicarbonate of ammonia.

A solution containing

0·0475 grm. tin, as bichloride,
and   0·0475 ,, arsenic, as arsenious acid,

was precipitated by sulphuretted hydrogen, the precipitate washed,

dissolved in yellow sulphide of ammonium, reprecipitated by hydro-
chloric and hydrosulphuric acids, agitated with cold sesquicarbonate
of ammonia and filtered; the filtrate contained a considerable quan-
tity of bisulphide of tin. In some cases, where even a rather large
amount of bisulphide of tin was mixed with the sulphide of arsenic,
the precipitate dissolved almost entirely in sesquicarbonate of ammo-
nia; and this is an additional instance of the strange alteration in the
reactions of tin, to which the presence of arsenic gives rise.

In order to separate the tin from the arsenic, I ultimately resorted
to a special method, which consisted in deflagrating the mixed sul-
phides (together, with the filter if necessary) with nitrate of potash,
digesting the fused mass with water, when part of the tin was left
behind in the insoluble residue, and acidulating the aqueous solution
with nitric acid, which, on heating, precipitated the whole of the
tin as binoxide. This precipitate, together with the residue left on
digesting the fused mass with water, was washed, dried, and ignited
with the filter; the ash fused with cyanide of potassium; the fused
mass digested with water; and the residual metal boiled with hydro-
chloric acid; the filtered solution was then tested with protochloride
of mercury for tin.

In a solution containing

$$0.095 \text{ grm. arsenic}$$
$$\text{and} \qquad 0.005 \quad \text{,,} \quad \text{tin}$$

the latter metal was very easily detected in this way.

The experiments detailed above led me to the following method for
the qualitative detection of tin, antimony, and arsenic, which is ap-
plicable to any solution in which these metals exist, provided that any
arsenic acid is first reduced to the state of arsenious acid.

The solution is largely diluted with water acidulated with hydro-
chloric acid, and sulphuretted hydrogen passed through it, to satura-
tion; the liquid is allowed to stand for some time in a warm place, and
the precipitate collected upon a filter; this precipitate is now washed
several times with water, and dissolved, with the aid of heat, in yellow
sulphide of ammonium; the solution thus obtained is mixed with an
excess of hydrochloric acid, and some strong solution of hydro-
sulphuric acid; the reprecipitated sulphides, collected on a filter,
well washed, transferred to a test-tube or small flask, and digested,
at about 82° (180° F.), with a saturated solution of sesquicarbonate
of ammonia, for about half an hour.

If the precipitate consisted of one of the sulphides of arsenic, it
would entirely dissolve, but it must then be remembered that the

presence of tin is by no means precluded; it may, however, be safely inferred that no antimony is present.

If there be any residue insoluble in sesquicarbonate of ammonia, it may contain bisulphide of tin and pentasulphide of antimony; it must be washed, on the filter, with sesquicarbonate of ammonia as long as the washings furnish any considerable yellow precipitate when acidulated with hydrochloric acid; it is then dissolved in a mixture of concentrated hydrochloric acid with about one-eighth of its bulk of concentrated nitric acid, using as little acid as possible. The solution is then mixed, in a beaker, with a considerable excess of sesquicarbonate of ammonia, and boiled for a few minutes. If no precipitate is produced, the absence of tin is certain, but if a precipitate is formed, it must be collected upon a filter for examination.

This precipitate may contain antimonic acid and binoxide of tin. It must be washed three or four times with sesquicarbonate of ammonia; dried; incinerated with the filter in a porcelain crucible; a little cyanide of potassium added to the ash; the mixture fused; the fused mass boiled with water; the reduced metal allowed to subside the supernatant liquid poured off; the reduced metal (remaining in the crucible) heated to boiling with concentrated hydrochloric acid; and the solution diluted with water, filtered, and tested for tin with protochloride of mercury.

The solution filtered from the precipitate produced by sesquicarbonate of ammonia in the nitro-hydrochloric solution of the sulphides of antimony and tin, will contain, under any circumstances, a part of the antimony; in order to detect this metal, the solution is acidified with hydrochloric acid (when, if much antimony be present, a precipitate of antimonic acid will be at first produced, and afterwards redissolved by an excess of acid); a stream of sulphuretted hydrogen is then passed through the solution, when the production of an orange precipitate will at once indicate the presence of antimony.

We have now to examine the solution obtained by digesting the original sulphides with sesquicarbonate of ammonia. It has been already shown that this solution may contain both bisulphide of tin and pentasulphide of arsenic; it is acidulated with hydrochloric acid, some hydrosulphuric acid added, and the precipitate divided into two equal parts, which are thrown upon separate filters, and washed, till the washings are free from chlorine.

One part of the precipitate is dissolved off the filter in warm ammonia, the solution evaporated to dryness on the water-bath, and

the residual pentasulphide of arsenic tested according to the method of Fresenius and Babo (reduced by cyanide of potassium and carbonate of soda, in a stream of carbonic acid).

The other portion of the precipitate, together with the filter, is dried, and deflagrated with nitrate of potash (the filter being cut into strips, and gradually added to the nitre in a state of fusion); the fused mass is poured from the porcelain crucible into one of iron, and when cool, boiled with water; nitric acid is then added till an acid reaction is produced; and the insoluble binoxide of tin collected upon a filter, dried, and tested for tin by the process described above for the examination of the former precipitate containing tin, which, in fact, might be advantageously examined together with this precipitate.

By this process, I have successfuly examined solutions containing tin, antimony and arsenic in the following proportions, the tin being present as bichloride, the antimony as terchloride, and the arsenic as arsenious acid dissolved in hydrochloric acid.

	Arsenic.	Antimony.	Tin.
1	95·0	2·5	2·5
2	2·5	2·5	95·0
3	5·0	5·0	90·0
4	47·5	5·0	47·5
5	47·5	47·5	5·0
6	5·0	47·5	47·5
7	90·0	5·0	5·0

In these cases, the unit, of which the above numbers are multiples, was 0·001 grm.

These and similar analyses have been often repeated, not only by myself, but by individuals who had no previous acquaintance with this method, and even by beginners in the study of analysis, and the result has shown me that, with comparatively little care, more certain analyses can be made by this method than by any other which has come under my notice.

The process seems rather a long one for the object in view; I have made several attempts to shorten it by detecting the arsenic and

tin in one operation, but the result, when small quantities of the metals were present, was not satisfactory.

After having framed a method upon which I felt that I could rely for the separation of these three metals, I determined to ascertain how far these could be separated from the other metals of this group, the members of which form sulphides insoluble in dilute acids.

The only method, I believe, employed in general analysis to effect this object, consists in heating the mixed sulphides with sulphide of ammonium containing an excess of sulphur, which is known to dissolve the sulphides of tin, antimony and arsenic, together with traces of sulphide of copper, and small quantities of bisulphide of platinum and tersulphide of gold. It was necessary, in order to ascertain the efficiency of this method, to analyse various mixtures containing known weights of the metals to be separated, and I accordingly conducted a series of experiments of this nature, some of which I may perhaps cite.

In these experiments the method of proceeding was as follows :'

The solution was acidified with hydrochloric acid, completely precipitated with sulphuretted hydrogen, the precipitate collected on a filter, well washed, and boiled for two or three minutes with the yellow sulphide of ammonium (prepared by the action of the air upon the hydrosulphate of sulphide of ammonium obtained by saturating solution of ammonia with sulphuretted hydrogen). The sulphide of ammonium solution was filtered off, and acidulated with hydrochloric acid, a quantity of a strong solution of hydrosulphuric acid was then added, and if the precipitated sulphur was in the slightest degree tinged, it was examined for antimony, tin, or arsenic, by the method given above.

On analysing a solution containing

<div style="text-align:center">

0·500 grm. of lead

and   0·005 ,,   of tin,

</div>

a part of the tin was found in the sulphide of ammonium solution, showing that the bisulphide of tin was not retained to any considerable extent by the sulphide of lead.

The tin was also found in the sulphide of ammonium solution, when there were present

<div style="text-align:center">

0·500 grm. bismuth

with   0·005 ,,   tin.

</div>

Also in the analysis of a solution containing

<div style="text-align:center">

0·100 grm. gold

and   0·005 ,,   tin.

</div>

The tin was likewise distinctly detected in a solution containing

| | 0·500 grm. platinum |
| and | 0·005 „   tin. |

When a solution containing

| | 0·500 grm. mercury |
| and | 0·005 „   tin |

was analysed in this way, no tin was found in the sulphide of am-
monium solution in two experiments.

When the same quantity of tin was present (0·005 grm.) together
with only 0·250 grm. mercury, the tin was only just recognised in
the sulphide of ammonium solution in two experiments.

In the examination of a solution containing

| | 0·500 grm. cadmium |
| and | 0·005 „   tin |

no tin was found in the sulphide of ammonium solution (in two
experiments), but when half the quantity (0·250 grm.) of cadmium
was present, the tin was just recognised distinctly, in two experi-
ments.

In the case of a solution containing

| | 0·01 grm. tin |
| and | 0·09 „   copper |

no tin was found in the sulphide of ammonium solution, but abun-
dance in the residue.

Even in the presence of only 0·03 grm. copper, the whole of the
tin was found in the residue.

When equal weights (0·01 grm.) of tin and copper were present,
most of the tin was found in the residue, although some was detected
in the sulphide of ammonium solution.

Very little tin was found in the solution in sulphide of ammonium
when

| | 0·03 grm. tin |
| and | 0·06 „   copper |

were employed.

When

| | 0·030 grm. tin |
| and | 0·075 „   copper |

were present (being in the proportion of 1 tin : 2·5 copper), very
little tin was found in the sulphide of ammonium solution.

In the case of

$$0.03 \text{ grm. tin}$$
and $$0.09 \quad \text{,,} \quad \text{copper}$$

a slight trace of tin was found dissolved in the sulphide of ammonium.

A scarcely perceptible trace was found in solution when

$$0.03 \text{ grm. tin}$$
and $$0.12 \quad \text{,,} \quad \text{copper}$$

were employed, and when the copper was increased to 0·135 grm. (being in the proportion of 1 tin : 4·5 copper), no tin was found in the sulphide of ammonium solution.

Many of the above experiments were repeated several times, with different specimens of sulphide of ammonium.

I also made several attempts to analyse a specimen of gun-metal (containing 90 copper and 10 tin) by dissolving in aqua regia, precipitating the diluted solution with sulphuretted hydrogen, and boiling the precipitated sulphides with sulphide of ammonium, but could not succeed in detecting the tin in the sulphide of ammonium solution, though it was easily found in the residue.

It appears, then, from these experiments, that the extraction of bisulphide of tin from a mixture of this sulphide with those of lead, bismuth, gold, platinum, mercury and cadmium, is sufficiently complete for most practical purposes; but that, in the case of the two latter sulphides, if no tin be found in the sulphide of ammonium solution, we can only conclude that the proportion of the tin to either the mercury or cadmium, is not *greater* than that of 2 to 100.

In presence of copper, however, it appears that no safe conclusion as to the absence of tin can be drawn from the circumstance that this metal is not found in the sulphide of ammonium solution of the sulphides.

In the analysis of a solution containing

$$0.005 \text{ grm. arsenic}$$
and $$0.500 \quad \text{,,} \quad \text{lead,}$$

the arsenic was detected in the sulphide of ammonium solution.

In a case where

$$0.005 \text{ grm. arsenic}$$
and $$0.500 \quad \text{,,} \quad \text{cadmium}$$

were present, arsenic was found in the sulphide of ammonium solution.

When   0·005 grm. arsenic
was present with   0·500 „   mercury,

a considerable proportion of the arsenic was found in the sulphide of ammonium solution.

In analysing a solution containing

              0·500 grm. bismuth
and   0·005 „   arsenic,

less arsenic than I expected was found in the sulphide of ammonium solution, in two experiments.

In the case of

              0·150 grm. gold
and   0·003 „   arsenic,

the latter was distinctly found in the sulphide of ammonium solution, though in smaller quantity than was expected.

The same was observed with

              0·500 grm. platinum
and   0·005 „   arsenic.

No arsenic was found in the sulphide of ammonium solution in the analysis of mixtures containing respectively :

              1·00 grm. copper
    with   0·01 „   arsenic
and

              0·90 grm. copper
    with   0·01 „   arsenic.

When   0·50 grm. copper
was present with   0·01 „   arsenic,

the latter metal was detected in the sulphide of ammonium solution, and was always found when smaller proportions of copper were present.

From these experiments, I inferred that the detection of arsenic is not influenced to any considerable extent by the presence of any metal of this group except copper, but that it is slightly affected by the presence of platinum, gold, bismuth, and lead.

If copper be present, the absence of arsenic, in any greater proportion than that of 2 to 100 copper, may be inferred if no arsenic is found in the sulphide of ammonium solution.

In the analysis of a solution containing

                          0·01 grm. antimony
        and   1·00 „   copper,

the antimony was distinctly found in the sulphide of ammonium
solution; and none was found in the residue left by sulphide of
ammonium

when   0·01 grm. antimony
was present with   0·10 „   copper.

Antimony was also distinctly found in the sulphide of ammonium
solution in the following cases :

          0·005 grm. antimony to 0·5 grm. lead
          0·005 „   „   0·5 „   bismuth
          0·005 „   „   0·5 „   cadmium
          0·005 „   „   0·5 „   mercury
          0·005 „   „   0·5 „ .platinum
          0·005 „   „   0·1 „   gold.

The detection of antimony, therefore, does not appear to be influ-
enced to any considerable extent by the presence of any other metal
of this group.

Since the presence of copper may, to a considerable extent, prevent
the detection of tin and arsenic by the ordinary method, it becomes
necessary, when copper is present, to examine for those metals in that
portion of the precipitate by sulphuretted hydrogen, which is insoluble
in sulphide of ammonium.

For the detection of arsenic in this portion of the precipitate, I
have usually resorted to the delicate test of Fresenius and Babo.*

The detection of tin, however, is more difficult; and the following
method has yielded me the most certain results.

The residue left by sulphide of ammonium is collected on a filter,
well washed, and boiled, as usual in the analysis of this precipitate,
with a mixture of concentrated nitric acid with two volumes of water,
to dissolve those sulphides which are soluble in this reagent; the
residue, which contains the binoxide of tin, is collected on a filter, and
washed; the filter, together with the precipitate, incinerated; the ash
fused with cyanide of potassium; and the fused mass boiled with
water.   The residuary metal is heated with hydrochloric acid, and the
solution tested with protochloride of mercury.

By this method the tin was easily discovered in the following
cases :

                    * Ann. Ch. und Pharm. XLIX, 287.

1. 0·01 grm. tin, 0·24 grm. mercury, 0·24 grm. lead, 0·24 grm. copper, and 0·01 grm. cadmium.
2. 0·01 „   tin, 0·25 grm. mercury, 0·25 grm. lead, and 0·50 grm. copper.
3. 0·01 „   tin and 0·09 grm. copper.
4. 0·01 „ · tin and 0·05 „   copper.
5. 0·01 „   tin and 0·03 „   copper.

In order perfectly to convince myself of the accuracy of this method for the detection of antimony, tin and arsenic, in the presence of considerable quantities of the other members of this group, I have made numerous analyses of solutions in which different proportions of these metals were present, and have not as yet met with a case where they escaped detection.

Two cases especially have engaged my attention, viz.:

<div style="text-align:center">

0·01 grm. antimony
0·50 „   copper
with   0·10 „   tin,

and

0·24 grm. lead
0·24 „   copper
0·24 „   mercury
0·01 „   bismuth
0·01 „   cadmium
0·01 „   antimony
0·24 „   arsenic,

</div>

and in the latter I have satisfied myself that no mistake can arise as to the presence of tin from the reactions of the other metals of this group.

I have, moreover, employed this method in analysing various alloys for technical purposes, and have never been able to detect any false affirmation or negation of the presence of antimony, tin, or arsenic.

Incidentally to this investigation, I often observed that considerable quantities of cadmium escaped detection; on examining into the cause of this disappearance of the cadmium, I found, that when tin was present, a large proportion of cadmium might be left undissolved, when the sulphides insoluble in sulphide of ammonium were treated with dilute nitric acid (a mixture of 1 volume of ordinary concentrated nitric acid and 2 volumes of water).

In the solution containing

$$
\begin{array}{ll}
& 0\cdot24 \text{ grm. mercury} \\
& 0\cdot24 \;\;\text{,,}\;\; \text{lead} \\
& 0\cdot24 \;\;\text{,,}\;\; \text{copper} \\
\text{and} & 0\cdot01 \;\;\text{,,}\;\; \text{cadmium}
\end{array}
$$

the cadmium was very easily found in the solution of the sulphides in dilute nitric acid.

When 0·01 grm. tin, however, was added to the above solution, the cadmium could not be detected in the nitric solution.

I found that the cadmium was always detected, when the residue left by nitric acid was incinerated and fused with cyanide of potassium, in the process for the detection of tin. During the fusion with cyanide of potassium, a red-brown sublimate of oxide of cadmium was formed on the lid of the crucible; this sublimate was dissolved in hydrochloric acid, and the solution mixed with strong solution of hydrosulphuric acid, when a fine yellow precipitate of sulphide of cadmium was obtained. I mention this circumstance with regard to the cadmium, because it seems to me probable, that the (at present) unaccountable disappearance of some of the other members of this group of sulphides may hereafter be traced to some similar cause, and that analysts will be induced rather to rely upon special tests in a particular search after individual metals, regarding the general course of analysis, merely as affording a systematic method of ascertaining what substances enter largely into the composition of the matter under examination.

I hope to be enabled, at some future time, to continue this investigation, in order, either to assure myself of the efficiency of the method which is at present generally followed in the analysis of the precipitate produced in acid solutions by sulphuretted hydrogen, or to point out where the difficulties are to be expected, and how they may be overcome.

These experiments were conducted in the laboratories of the Royal College of Chemistry; and it gives me great pleasure to express my sincere thanks to Professor Hofmann, for the kind advice and assistance which I have received from him during their progress.

I subjoin, in a tabular form, the method which I now adopt for the detection of tin, antimony and arsenic, in the precipitate produced by sulphuretted hydrogen in a solution previously acidulated with hydrochloric acid.

The precipitate is well washed, and boiled for some minutes with yellow sulphide of ammonium.

The residue is washed till the washings contain no chloride of ammonium, and boiled with dilute nitric acid (1 vol. concent. acid and 2 vols. water).

The residue is collected on a filter, dried, and incinerated; the ash fused with cyanide of potassium; the fused mass boiled with water; the reduced metal heated to boiling with concentrated hydrochloric acid; and the solution diluted with water, filtered, and tested with protochloride of mercury. A white or grey precipitate (according to the quantity of tin) indicates the presence of tin.

The solution is examined as usual.

The solution is acidulated with hydrochloric acid, and mixed with some strong hydrosulphuric acid. The precipitated sulphides are washed, and digested at a gentle heat, with a saturated solution of sesquicarbonate of ammonia, for about half an hour, and filtered.

The residue is washed with solution of sesquicarbonate of ammonia, till the washings give no considerable yellow precipitate with hydrochloric acid, and dissolved off the filter in hot hydrochloric acid with a little nitric acid. The solution is mixed with excess of sesquicarbonate of ammonia and boiled for two or three minutes.

The precipitate is washed with a little sesquicarbonate of ammonia, dried, and incinerated, the ash fused with cyanide of potassium; the fused mass boiled with water; the reduced metal allowed to subside; the aqueous solution decanted; the metal heated to boiling with concentrated hydrochloric acid; the solution diluted with water, and tested with protochloride of mercury. White or grey precipitate; presence of tin.

The solution is slightly acidulated with hydrochloric acid, and sulphuretted hydrogen passed through it. If the precipitate has a pure orange colour, the presence of antimony may be inferred; but, in any other case, the precipitate should be collected on a filter; washed; boiled with concentrated ammonia; a few bubbles of sulphuretted hydrogen passed; and the solution filtered. The filtrate is acidulated with hydrochloric acid, and sulphuretted hydrogen passed. Orange precipitate indicates antimony.

The solution is acidulated with dilute hydrochloric acid, a little hydrosulphuric acid added, and the resulting precipitate washed and divided into two parts.

One part is dried and deflagrated (with the filter, if necessary), with nitrate of potash, the fused mass boiled with water; and the aqueous solution acidulated with dilute nitric acid. A white precipitate will indicate the presence of tin, which may be confirmed by drying this precipitate upon a filter; incinerating the latter; fusing the ashes with cyanide of potassium; washing the reduced metal; and boiling with hydrochloric acid. The hydrochloric solution may then be tested with protochloride of mercury.

The remainder of the precipitate is dissolved off the filter in warm ammonia; the solution evaporated to dryness on a water-bath; and the residue tested for arsenic according to the method of Fresenius and Babo.

X.—*Researches on the Constitution of Organic Acids.*

By M. Charles Gerhardt.

COMMUNICATED BY DR. WILLIAMSON.

The experiments which I am about to lay before the Society, are intended as the commencement of a series of researches undertaken with a view to find a general expression for the molecular constitution of organic acids ; or rather, to explain the properties of double decomposition belonging to this class of compounds. I endeavoured to connect organic acids, numerous and various as they are, by a general formula which would be for them what the formula of ammonia is for the organic alkalies ; in a word, I sought among the compounds of mineral chemistry for a body which is reproduced by simple substitutions of one or other of its elements, as ammonia is repoduced from the organic alkalies by substitution of the groups methyl, ethyl, phenyl, &c., by one, two or three atoms of hydrogen. This term of comparison, this body, typical of acids, I believe I have found.   For the understanding of my experiments, it is necessary to name this body at once.   It is *water,* in the molecule of which I assume one atom of oxygen and *two* atoms of hydrogen,

$$\left.\begin{array}{c} H \\ H \end{array}\right\} O,$$

two atoms which may be replaced by simple metals, or by complex groups like methyl, ethyl, &c.

The results obtained a short time ago on this subject by Dr. Williamson in England, and by M. Chancel in France, are well known.   These chemists have indeed proved that alcohol, common ether, and their homologues, represent molecules of water in which the two atoms of hydrogen are partly or wholly replaced by complex groups ; so that common alcohol represents water in which half the hydrogen is replaced by the group ethyl $(C_2 H_5 = Et)$

$$\left.\begin{array}{c} Et \\ H \end{array}\right\} O,$$

whilst common ether represents the same molecule of water in which the two atoms of hydrogen are so replaced :

$$\left.\begin{array}{c} Et \\ Et \end{array}\right\} O.$$

According to this theory, now almost universally adopted, the

compound formed by replacing one atom of hydrogen in alcohol by potassium, is to be considered as water in which the two atoms of hydrogen are replaced, one by ethyl, the other by potassium :

$$\left.\begin{array}{c} Et \\ K \end{array}\right\} O.$$

It may be called potassic ethylate, that is, the potassium-salt of an acid which is nothing else than common alcohol, a weak acid evidently, for water decomposes its salt into alcohol and caustic potash. In like manner, common ether is the ethyl-salt of this ethylic acid. The starting point for my experiments was supplied by this analogy, together with the fact that ethylic acid gives rise to a chloride (hydrochloric ether, or chloride of ethyl) when acted upon by pentachloride of phosphorus; and that, according to M. Cahours' experiments, various organic acids, such as benzoic, nitrobenzoic, cuminic, anisic, and cinnamic, experience an exactly similar change by the influence of the same reagent.

As potassic ethylate, in reacting on ethylic chloride, forms potassic chloride and ethylic ethylate, that is common ether (the experiment is well known), I sought with the chloride of one of the above-mentioned acids, and the potassium- or sodium-salt of the same acid to obtain a body corresponding to common ether; in other words, I sought to obtain the anhydrous acid, as ether itself is nothing but alcohol minus water.

With sodic benzoate and benzoic chloride, the experiment succeeds perfectly well. The soda-salt should be dried and mixed with an equivalent weight of the chloride; the mixture is then heated to 130° C. in a sand-bath, at which temperature a limpid solution is formed, which decomposes with deposition of chloride of sodium when heated a few degrees higher. The action is then complete, not a trace of gas is evolved, and the fearful smell of the benzoic chloride entirely disappears. The product suspended in cold water, and washed with carbonate of soda, leaves a white substance without odour, and perfectly colourless, which analysis shows to be anhydrous benzoic acid :

$$C_{14} H_{10} O_3,$$
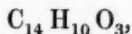
that is to say, benzoic benzoate; for it is to benzoic acid what ether is to alcohol, and if benzoic acid is represented similarly to alcohol, as water in which one atom of hydrogen is replaced by the group benzoyl $C_7 H_5 O = Bz$:

$$\left.\begin{array}{c} Bz \\ H \end{array}\right\} O,$$

then my new substance is water, in which the two atoms are similarly replaced:

$$\left.\begin{array}{c} \text{Bz} \\ \text{Bz} \end{array}\right\} \text{O}.$$

The following are the properties of this anhydrous benzoic acid. It is obtained in the form of beautiful oblique prisms, which melt at $33°$ C.; they are volatile without decomposition, insoluble in water, soluble in alcohol and ether; these solutions are perfectly neutral. When dissolved in hot alcohol, the acid is deposited, on cooling, in the form of an oil, which remains a long time without solidifying; the same thing occurs when the substance is distilled; in which case it sometimes remains liquid for several hours. Cold water has no action upon it; but boiling water transforms it, little by little, into common benzoic acid. The same transformation is effected in a few moments by boiling ammonia. Alcohol itself transforms anhydrous benzoic acid in the course of time into benzoic ether; the group benzoyl is then replaced by the group ethyl.

Having succeeded so well with the chloride of benzoyl and benzoate of soda, I made similar experiments with other chlorides and other salts. I did not of course limit myself to cases of the action of chlorides upon salts of the same acid; but took the chloride of benzoyl, and successively, salicylate, cuminate, cinnamate and acetate of potash. Benzoic salicylate, cuminate and cinnamate were thus formed. These products are for the most part very fusible solid bodies, or oils heavier than water, without smell, and are rapidly decomposed by the alkalies in a similar manner to benzoic acid with alkalies. Several of them are not volatile without decomposition; thus the benzoic salicylate, when distilled in a moist state, decomposes into salicylic acid and a neutral body, fusible at $72°$ C., which is the true benzoyl,[*] isomeric with the benzoyl of M. Laurent:

[*] There can be no doubt that this substance is identical with the compound discovered by Ettling among the products of distillation of benzoate of copper, which was subsequently analysed by Dr. Stenhouse, who gives the same formula, namely,

$$C_{14} H_5 O_2.$$

Stenhouse states that the fusing-point of this substance is $70°$, and that it yields benzoate of potassa when heated with solid hydrate of potassa, hydrogen being evolved. The compound

$$C_{14} H_5 O_3$$

obtained by Ettling among the products of distillation of salicylite of copper, and described by him by the name of *parasalicyl*, has the same composition as M. Gerhardt's benzoic benzoyl, but differs from it in its properties, fusing as it does at $127°$, and being, as it appears, only slightly acted upon by potassa. Probably this substance stands to benzoic benzoyl in the same relation as salicylous acid to benzoic acid.—A. W. H.

$$C_{14} H_{10} O_2 = Bz\ Bz,$$
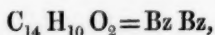
that is to say, it is to hydrogen, H_2, what hydrated benzoic acid and anhydrous benzoic acid are to water. Hydrate of potash in a state of fusion converts it into benzoate, with evolution of hydrogen.

I will limit myself for the moment to this summary announcement of my experiments, and propose following them out with all the care which the subject requires.

If a general conclusion may now be drawn from these results, I would say that they destroy the kind of privilege hitherto enjoyed by a small number of bodies known by the generic name of alcohols, of being susceptible of joining other organic bodies. Alcohols and hydrated acids are evidently bodies of the same kind. Philosophically, alcohols, acids, ethers, salts, and anhydrous acids, may be reduced to the same generic formula—to the formula of water, in which 1 or 2 atoms of hydrogen are replaced, either by simple metals or by hydrocarburetted groups (methyl, ethyl, phenyl, &c.), or else by oxygenated groups (benzoyl, cuminyl, acetyl, &c.)

I have now succeeded in preparing anhydrous acetic acid in a state of perfect purity, and giving by analysis numbers exactly agreeing with those calculated from its formula. The following is the method of preparing it : Acetate of potash is fused, so as to expel all water of crystallization, and is then mixed in a small retort with about half its weight of benzoic chloride. On the application of a gentle heat, the reaction speedily occurs—benzoic acetate being no doubt formed at first. But the reaction does not stop there. A limpid body distils over, with a very powerful smell, reminding of acetic acid and flowers of " acebessine." On rectification, this liquid boils constantly at 137° C.; it falls to the bottom in water, and does not mix with it at once, but only after continued agitation. Hot water dissolves it at once, with production of acetic acid. The following figures show the result of combustion :

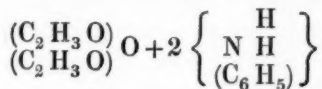|	Analysis.	Calculation.
Carbon	46·87	47·05
Hydrogen	5·95	5·88

It is therefore $C_4 H_6 O_3$ or, rather $\begin{array}{c} C_2 H_3 O \\ C_2 H_3 O \end{array} O*$

This anhydrous acetic acid evolves great heat on mixture with dry
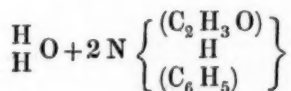
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* A similar view regarding the constitution of acetic acid has been proposed by Professor Williamson.—Ch. Soc. Qu. J.—Eds.

aniline; the mixture solidifies entirely on cooling. If an excess of aniline is avoided, only one body is produced, crystallizing in beautiful nacreous plates. This body is shown by analysis to be acetaniline.

It is remarkable that no salt of aniline is formed at the same time. We must therefore consider the action as consisting of a double decomposition between the aniline and the anhydrous acid ; thus

$$\left.\begin{array}{l}(C_2 H_3 O) \\ (C_2 H_3 O)\end{array}\right\} O + 2 \left\{\begin{array}{l} H \\ N \; H \\ (C_6 H_5)\end{array}\right\}$$

forms

$$\left.\begin{array}{l} H \\ H\end{array}\right\} O + 2 N \left\{\begin{array}{l}(C_2 H_3 O) \\ H \\ (C_6 H_5)\end{array}\right\}$$

We must, I think, consider amides and anilides as ammonia in which more or less hydrogen is replaced. I am now engaged in the investigation of this point.

Amidogen-acids would correspond to hydrated oxide of ammonium.

XI.—*Note on the Preparation of Carbonate of Amyl.*

By John A. Bruce,

OF THE ROYAL COLLEGE OF CHEMISTRY, LONDON.

Carbonate of amyl has been lately examined by Mr. Medlock, whose experiments have been described to the Chemical Society.* He obtained this compound by a method which had not yet been used for the preparation of carbonic ethers, namely, by the action of phosgene gas upon fusel-oil, and subsequent decomposition of the chlorocarbonate formed, under the influence of heat, in the presence of water. The process which originally had furnished the carbonate of the ethyl-series, and which consists in distilling the oxalate with potassium, has never been applied to the amyl-series.

The reaction of potassium upon the ether-oxalates being still but

* Chem. Soc. Qu. J. I, 368.

imperfectly understood, Dr. Hofmann requested me to repeat the
experiment with oxalate of amyl, in order to obtain some additional
data for a more correct interpretation of the phenomena attending the
decomposition.

Potassium, when coming in contact with perfectly dry oxalate of
amyl, is rapidly attacked, the liquid becomes warm, and a brown
mass forms around the metallic globules, whilst a colourless inflam-
mable gas is disengaged. The reaction, however, soon slackens,
and only commences again on heating the liquid. On distilling
the fluid, a brown residue was obtained, consisting chiefly of
carbonate of potash and charcoal, while a pale-yellow distillate
passed over; this liquid, when rectified with a thermometer, was
found to consist of not less than four different substances. It
began to boil at 130° C. (266° F.), at which temperature chiefly
fusel-alcohol distilled; the boiling-point then rapidly rose to about
225° C. (433·4 F.), when it became stationary for a very considerable
time, indeed until three-fourths of the whole had passed over. The
liquid distilling at this temperature was pure carbonate of amyl, as
proved by the analyses hereafter to be detailed. The mercury then
again rose until the temperature was 260° C. (500° F.), when it
became once more stationary, but only for a short period, evidently
because a small portion of undecomposed oxalate of amyl, which
boils at this temperature, was still present in the liquid. After this
had been evaporated, a viscous, somewhat dark residue, having a
very powerful odour, remained in the retort.

The portion which had been collected between 223° and 226° C.
(433·4° and 438·8 F.) was repeatedly redistilled, until a liquid of a
constant boiling-point at 226° C. (438·8 F.) was obtained, which at
15·5° C. (60° F.) had a sp. gr. of 0·9065. When submitted to
combustion, it gave the following results :

I.   1·91 grains of substance gave :
     4·60   „   „   carbonic acid, and
     1·95   „   „   water.
II. 2·05   „   „   substance gave :
     4·90   „   „   carbonic acid, and
     2·10   „   „   water.

Percentage-composition :

	I.	II.
Carbon. .	65·68	65·12
Hydrogen .	11·30	11·31

These numbers agree pretty closely with the formula,

$$C_{10} H_{11} CO_3,$$
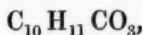
as may be seen in the following comparison of the theoretical numbers with the results of the experiments:

			Theory.		Mean of the Experiments.
11 eqs.	Carbon . .	66	65·34		65·40
11 „	Hydrogen .	11	10·89		11·35
3 „	Oxygen . .	24	23·77		—
		101	100·00		

Carbonate of amyl may be produced by the action of potassium or sodium (the latter metal was indeed employed in most of my experiments) upon oxalate of amyl with great facility, and to any extent; its preparation in this reaction is not attended with the same difficulties which we experience in performing the experiment in the ethyl-series. The actual process, however, which gives rise to its formation remains still doubtful, although the preceding experiments have furnished a new element for its correct interpretation, namely, the observation of a large quantity of amyl-alcohol being reproduced during the reaction—a reproduction which has escaped notice in the preparation of the carbonic ether *par excellence,* on account of the solubility of the ethyl-alcohol in water.

XII.—*New Formation of Salicylic Acid.*

By H. GERLAND.

Mr. Gerland has been lately engaged in my laboratory with a comparative investigation of the three isomeric acids, namely: Zinin's benzamic acid, Fritzsche's anthranilic acid, and Chancel's carbanilic acid, induced chiefly by the frequently asserted view of these acids being identical.

According to certain theoretical views which I have already

stated,* I considered myself justified in doubting the identity of benzamic with anthranilic acid, it being more probable, however, that anthranilic acid is identical with carbanilic acid, and that it stands in the same relation to carbonic acid as carbamic acid. This assumption is based upon the view that benzoic acid is an oxide of the conjugate benzoyl-radical $(C_{12} H_5)^\frown C_2$, namely, $HO, (C_{12} H_5)^\frown C_2 O_3$, that nitrobenzoic acid $HO, \left(C_{12} \left\{ {H_4 \atop NO_4} \right. \right)^\frown C_2 O_3$ contains a secondary benzoyl-radical, in which NO_4 replaces H; and that the nitro-benzoyl of nitrobenzoic acid is converted by treatment of the latter with sulphide of ammonium, into amido-benzoyl of the formula $\left(C_{12} \left\{ {H_4 \atop H_2N} \right. \right)^\frown C_2$.

Benzoic acid . . $HO (C_{12} H_5)^\frown C_2, O_3$

Nitrobenzoic acid $HO \left(C_{12} \left\{ {H_4 \atop NO_4} \right. \right)^\frown C_2, O_3$

Benzamic acid
(Amido-benzoic acid) $HO \left(C_{12} \left\{ {H_4 \atop H_2N} \right. \right)^\frown C_2, O_3.$

According to this view, benzamic acid would be benzoic acid with 1 equivalent of hydrogen in its radical, replaced by 1 equivalent of amidogen, while the isomeric anthranilic acid

$$HO . C \left\{ C_{12} {O \atop H_5 \atop H} \right\} N \right\} ; CO_2$$
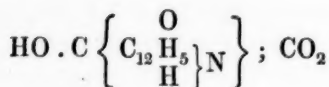
has the chemical constitution of carbamic acid

$$HO . C \left\{ {O \atop H_2 N} \right\}, CO_2,$$
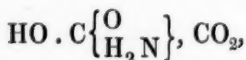
and is only distinguished from the latter by containing anilidogen instead of amidogen.

The experiments performed by Mr. Gerland, which he will shortly communicate in detail, have proved that benzamic and anthranilic acid are in fact distinct acids, and that they not only differ materially in their chemical properties, but also yield under similar influences, perfectly different (sometimes very interesting) products of decomposition.

* Chem. Soc. Qu. J. IV, 73.

While anthranilic acid is always deposited from the hot aqueous solution in needles, sometimes an inch in length, benzamic acid can only be obtained from its hot saturated aqueous solution as an indistinctly crystalline mass. The salts of the two acids exhibit much similarity in appearance; those of benzamic acid are however, generally speaking, much more soluble than the corresponding salts of anthranilic acid.

The difference of the two acids is most clearly shown in their comportment with potash, sulphuric and nitrous acid.

Anthranilate of potash, when heated with hydrate of potash, yields aniline; the benzamate does not yield a trace of this body.

While strong sulphuric acid converts anthranilic acid into sulphanilic acid, with evolution of carbonic acid gas; benzamic acid, on the other hand, dissolves in it without evolution of gas, forming a violet solution.

If nitrous acid (prepared by acting on arsenious acid with nitric acid) is passed through a dilute warm aqueous solution of anthranilic acid, till no more nitrogen is evolved, it remains clear, and yields, on evaporation, fine long needles of an acid free from nitrogen, and possessing the composition and properties of salicylic acid.

With salts of sesquioxide of iron it yields the characteristic violet colour produced by salicylic acid, under the same circumstances, and on dry distillation, a considerable quantity of phenol is produced, a portion of the acid subliming unchanged.

The conversion of anthranilic acid into salicylic acid, by means of nitrous acid, which you anticipated in your paper* on the action of nitrous acid on the amidogen-bases, takes place according to the following equation :

$$HO \cdot \underbrace{C_{14} H_6 NO_3}_{\text{Anthranilic acid.}} + NO_3 = HO \cdot \underbrace{C_{14} H_5 O_5}_{\text{Salicylic acid.}} + HO + 2\,N.$$
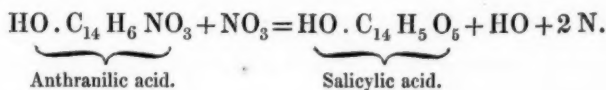
A dilute aqueous solution of benzamic acid also undergoes a change when exposed to the action of nitrous acid; not a trace of salicylic acid is, however, formed. An alcoholic solution of benzamic acid, through which nitrous acid is passed, becomes red, then turbid, and deposits a red crystalline body, insoluble in water and alcohol, but readily dissolved by ammonia and potash, which Mr. Gerland is at present examining.

If benzamic acid retains the constitution of benzoic acid (*i. e.* if it

* Chem. Soc. Qu. J. III, 235.

is amido-benzoic acid), it is probable that a benzoic acid would be obtained by its decomposition with nitrous acid, in which one equivalent of hydrogen in the radical is replaced by one equivalent of oxygen, namely, $HO,\left(C_{12}\left\{{H_4 \atop O}\right)^\frown C_2, O_3\right.$

The results of all experiments which have at present been conducted in this direction would appear to favour this view.

XIII.—*Chemical Memoranda.*

By ROBERT WARINGTON.

In laying the present short notices before the Chemical Society, I do it with the impression that the example may be useful as a means of registering a great number of very interesting and sometimes important facts and observations, which, taken in their isolated state, would not afford sufficient matter for their being arranged in the form of a paper, and therefore are generally laid aside, and frequently altogether lost to science ; whereas, if they were collected and arranged as a series of memoranda, they would serve to occupy profitably a few pages of our Transactions, with useful practical observations, and give rise at the meetings of the Society to much valuable discussion. Under this impression, therefore, I have made bold to endeavour to pioneer the way, in a path which I hope to see followed by many of our working members.

The first memorandum I shall submit to your attention is :

On a curious form of Crystallization of Iodide of Potassium.

In the preparation of this salt on the large scale, crystals are at times obtained presenting a very curious appearance, namely, that of a cubic needle or prism, of considerable length, and of varying diameter, and apparently formed by the superposition of cube upon cube. The specimens to which I would more particularly direct your attention, were procured some years since, and have become much injured and fractured ; but sufficient of them remains to demonstrate fully the following details of measurement. Two only of these crystals were selected for this purpose ; but I may mention that many similar ones were obtained at the same time as these. The first specimen had a total length of 4·40 inches, which was composed of the following divisions :

At its point of attachment to the general mass of salt, its diameter was :

$\frac{6}{40}$ of an inch, which continued for $\frac{42}{40}$ of an inch ; it then decreased to $\frac{5}{40}$,, ,, ,, $\frac{85}{40}$,, ,,

,, ,, $\frac{3}{40}$,, ,, ,, $\frac{33}{40}$,, ,,

,, ,, $\frac{2}{40}$,, ,, ,, $\frac{16}{40}$,,

where the crystal terminated.

$$\frac{176}{40} = 4\cdot40 \text{ inches.}$$

The second specimen was found to give the following measurements : Its entire length was $2\,\frac{7}{40}$ of an inch, and the diameter of the cubic needle, at its junction with the rest of the crop, was :

$\frac{7}{40}$ of an inch, which continued for $\frac{14}{40}$ of an inch ; it then decreased to $\frac{5}{40}$,, ,, ,, $\frac{25}{40}$,, ,,

,, ,, $\frac{4}{40}$,, ,, ,, $\frac{48}{40}$,,

Total length . . . . $\frac{87}{40} = 2\,\frac{7}{40}$ inches.

It will be evident, therefore, that these crystals exhibit certain distinct and strongly marked intervals of decrease in their stages of progression ; and this decrease in the diameter of the cube is sudden and abrupt, forming at that point sharp and well-defined angles, and not passing gradually from one dimension into the other as it elongates. It will be noticed, also, in looking over the measurements, that a perfectly symmetrical cubic arrangement is maintained throughout their whole extent, and that the intervals of length correspond exactly to a multiple of the diameters of the cubes.

These crystals are most frequently obtained when the solutions from which they are deposited are rather alkaline.

<div align="center">MEMORANDUM II.</div>

On a method of detecting, qualitatively, small quantities of Oxide of Copper in solution.

This operation depends upon the solubility of the ferrocyanide of copper in an excess of a solution of ammonia, and its deposition with its well-marked characteristic appearances as the ammonia evaporates. Thus, supposing a frequently occurring case, where the oxide of copper, in very small quantity, is in solution with oxide of iron, and that these metals have been brought to their highest state of

oxidation; ammonia is next added in excess, and then a few drops of a solution of the ferrocyanide of potassium, and the whole thrown upon a filter. As the ammonia escapes from the filtrate by standing, and free exposure to the air, the red ferrocyanide of copper will be deposited, and if the experiment be made in a shallow white porcelain dish, the result will be very distinct and characteristic, and on carefully decanting the fluid, will be found on the white surface. In many cases, the process of filtration may be dispensed with altogether, as the suspended peroxide of iron does not in the least interfere with the deposition of the ferrocyanide of copper from the solution. I have found this test give unerring indications in cases where no trace of blue colour could be distinguished in the ammoniacal solution, and where no precipitation could be procured by hydrosulphuric acid gas or the action of a voltaic circuit.

When organic colouring matter is present, this form of test is also very useful, as in vinegars, &c., and it was in a case of this kind which came under my notice some years since, that I was induced to put it more fully into practice. A party was seeking to recover compensation for the destruction of some valuable meadow-lands, from the action, it was affirmed, of the waste waters from some copper mines. These meadows owed their luxuriance, and consequent value, to a periodic inundation by the water from the granite moors of that part of Cornwall. Several copper mines had, however, been opened on these high lands; and from the scarcity of water, it was retained at the mines for some time, being used over and over again for stamping and dressing the ores, until it became, as a natural consequence, highly charged with metallic impurities. In this state it was, at certain intervals of time, discharged in large quantities down the valley, overflowing the banks of the stream and causing the destruction complained of.

The great object, in a chemical point of view, was to trace the cause of the injury into the substance of the injured herbage, the dead grass; and this I found could be readily and satisfactorily accomplished by means of the test now indicated.

Our late respected President, Mr. Phillips, to whom I mentioned this mode of testing some years since, introduced it into his translation of the London Pharmacopœia.

MEMORANDUM III.

Some additional observations on the Green Teas of commerce.

Since the publication of my last communication on this subject, read before the Society on May 19th, 1851, a series of microscopical and chemical examinations have been published* which have induced me to institute some additional experiments, the results of which may not be without interest to some of the members of the Society, particularly as they tend to remove a curious anomaly that has lately arisen. In the series of examinations alluded to, it is stated that several of the specimens of green tea submitted to investigation, were coloured with indigo mixed with porcelain clay; and this is followed by an examination of some of the colouring materials themselves used at Canton for this purpose, and which had been obtained from the museum at Kew Gardens. As I had stated† that, up to that period, no sample in which indigo had been employed as an artificial colouring agent for green teas had come under my notice, I felt it incumbent on me to investigate the matter. For this purpose I applied to Sir W. Hooker on the subject, and he allowed me in the handsomest manner to take from the cases in the museum, small portions of the materials for examination, and also favoured me with the loan of the manuscript Journal of Mr. Berthold Seeman, by whom the specimens had been collected while at Canton, as Naturalist of H.M. ship 'Herald,' then on a survey in that quarter of the globe. As these documents have been since published, and as the subject opens some interesting particulars, I have taken the liberty of appending his account in his own words.‡ Mr. Seeman here dis-

* The Lancet, August 9th, 1851.
† Qu. J. Chem. Soc. IV, p. 156.
‡ Hooker's Journal of Botany and Kew Garden Miscellany, No. 37, for Jan., 1852: "In the 'Manual of Scientific Inquiry' you ask whether, in the northern provinces of China, indigo or any other vegetable dye is used in colouring green tea? Whether different processes of dyeing are pursued in the north from those of the south, I cannot say, but it is certain that around Canton, whence great quantities are annually exported, the green tea is dyed with Prussian blue, turmeric and gypsum, all reduced into fine powder. The process is well described by Sir J. F. Davis ('The Chinese,' III, 244), who, however, falls into the strange mistake of supposing the whole proceeding of colouring to be an adulteration, and leaves his readers to infer that it is only occasionally done in order to meet the emergency of the demand; while it is now very well known that all the green tea of Canton has assumed that colour by artificial dyeing. I had heard so much about tea, copper-plates, picking of the leaves, rolling them up with the fingers, boiling them in hot water, &c., that I became anxious to see with my own eyes

tinctly states, that around Canton the *green tea* is dyed with *Prussian blue, turmeric, and gypsum;* that, in the manufacture he inspected, the *dyes above mentioned* were added; and he gives their proportions. That there was *no concealment* or mysterious proceeding; that one of the great merchants conducted him over his own and also another manufactory, and that everything was conducted openly and exhibited with great civility. And yet, strange to say, Mr. Seeman appears to have been deceived notwithstanding all this; for on submitting these materials to the action of chemical tests, there could be no doubt that they consisted of indigo, of a very inferior quality, and leaving a very large proportion of inorganic matter by calcination, and of porcelain clay. It is also curious that the very case selected by Mr. Seeman to illustrate the processes, is the conversion, by means of this facing or glaze, of a low quality of black tea (Bohea Saushung) valued at about 4*d.* to 6*d.* the pound, into high quality green teas valued at from 1*s.* to 1*s.* 6*d.* the pound; but although Mr. Seeman does not allow this to be an adulteration, yet surely he cannot deny that it is a fraud.

Another very good method which I have lately employed of removing the colouring matter from the surface of green teas for the purpose of microscopical investigation, and one attended with very little trouble, is to take a piece of cream-coloured wove paper, or

the process of manufacture, of which the various books had given me such a confused idea. One of the great merchants conducted me not only to his own, but also to another establishment, where the preparation of the different sorts was going forward. There was no concealment or mysterious proceeding, everything was conducted openly, and exhibited with the greatest civility; indeed, from all I saw in the country, I am almost inclined to conclude that either the Chinese have greatly altered, or their wish to conceal and mystify everything, of which so much has been said, never existed.

"The tea is brought to Canton unprepared. After its arrival it is first subjected to cleaning. Women and children are employed to pick out the pieces of twigs, seeds, and other impurities with which it happens to be intermixed. The only sorts which may be called natural are those gathered at different seasons; the rest are prepared by artificial means.

"Without entering into a description of all these processes, it may suffice to take one as an example. A quantity of Bohea Saushung was thrown into a spherical iron pan kept hot by means of a fire beneath. These leaves were constantly stirred about until they became thoroughly heated, when the dyes above mentioned were added, viz., to about twenty pounds of tea, one spoonful of gypsum, one of turmeric, and two or even three of Prussian blue. The leaves instantly changed into a bluish-green, and, having been stirred for a few minutes, were taken out. They, of course, had shrivelled, and assumed different shapes from the heat. The different kinds were produced by sifting. The small, longish leaves fell through the first seive, and formed Young Hyson, while those which had a roundish, granular shape, fell through last, and constituted Choo-cha, or Gunpowder."

paper free from blue colouring material, and having breathed on its surface or rendered it slightly damp, to pour the sample of tea under examination, from the containing paper or vessel upon it.   On then removing it back again, a quantity of the facing powder will be found adhering to the surface of the paper; and on placing it under the microscope, it will be found studded with the colouring materials used, and the blue particles can be subjected to the action of chemical tests with the greatest ease, by placing a minute drop of the reagent on the granules with the end of a small stirring rod, or slip of glass, and noting the effect.

<div align="center">MEMORANDUM IV.</div>

A modification of the ordinary process of sublimation in a straight tube.

In examining the blue colouring material used for green tea taken from the Kew Museum so as to demonstrate its being indigo, I was led to try a modified arrangement in the ordinary method of using the straight tube for sublimation.   It consists simply in introducing the material to be examined into a small capillary tube, of such an external dimension that it can be easily passed into the interior of another tube, which should be of hard white glass.   By this means the substance can be placed over whatever part of the external tube the operator may desire, at the same time avoiding any risk of soiling the part of the external tube on which the sublimate is to be condensed, and with the power of withdrawing the material at any time for the removal of condensed moisture, or only matter, as also of shifting its position during the operation.   The experiment being completed, the internal tube is withdrawn, and both the fixed residue and the volatile constituents can be readily submitted to chemical agents, or put by for future investigation.

I have since employed this arrangement in various other cases, as in the detection of arsenic and corrosive sublimate in cases of poisoning, with complete success.

XIV.—*On the Action of Ammonia upon Binoxysulphocarbonate of Amyl.*

By MATTHEW W. JOHNSON,

ASSISTANT IN THE LABORATORY OF ST. BARTHOLOMEW'S HOSPITAL.

Chemists are acquainted with the singular compound which M. Desains obtained by the action of iodine upon xanthate of potash, and described under the somewhat lengthy name of binoxysulphocarbonate of ethyl. They likewise recollect the experiments of M. Debus, who submitted this compound to the action of ammonia, in order to obtain, if possible, a more definite view regarding its constitution, which is still open to discussion. These experiments led to the discovery of a new substance, which M. Debus terms xanthamide, and which is formed in this reaction, together with xanthate of ammonia. The corresponding term in the amyl-series being still unknown, Dr. Hofmann suggested to me the preparation and study of this substance, while at the Royal College of Chemistry, in the laboratory of which Institution, the experiments about to be described were carried out.

In preparing binoxysulphocarbonate of amyl, Desains' process, slightly modified, was successfully employed. To hydrate of potash, crushed to a coarse powder in a mortar, fusel-oil and excess of anhydrous bisulphide of carbon are added, and the mixture triturated until a soft yellow mass results. A small quantity of a red oily liquid is generally found disseminated through it.

Amyloxanthate of potash thus prepared, is placed in a flask with bisulphide of carbon, sufficient in quantity to convert it into a very thin paste. Iodine is then introduced, which is immediately decolorized, with evolution of heat. On agitation, a grey mixture is formed, consisting of roundish granules of iodide of potassium, and a yellow mobile liquid. The whole, thrown on a filter, and washed with bisulphide of carbon, yields a filtrate, which, on distilling off the bisulphide of carbon, leaves the binoxysulphocarbonate of amyl, a yellow oily liquid, which is thus prepared, in considerable quantity, with the greatest ease, and sufficiently pure.

This compound was treated with ammonia, in order to obtain the substance corresponding to M. Debus's xanthamide. The plan which first suggested itself, was to pass dry ammoniacal gas through an alcoholic solution of the substance, and to separate the amide from the ammoniacal salt simultaneously generated, by evaporating

to dryness, and exhausting by means of ether, a mode of separation quite successful with regard to xanthamide. This method, however, failed, from the fact that the new compound produced in this reaction, which I shall designate by the term *Xanthamylamide*, is only slightly more soluble in ether than the accompanying ammonia-salt, which, as proved by subsequent analysis, was amyloxanthate of ammonia. The process finally adopted, was to digest the binoxysulphocarbonate of amyl with a concentrated aqueous solution of ammonia, at a slightly elevated temperature. In the course of a few minutes the mixture becomes turbid, sulphur is deposited, and a yellow liquid, through which oily particles are seen suspended, floats above. Four or five hours suffice to accomplish the reaction. When 1 part, by bulk, of binoxysulphocarbonate of amyl is treated with 3 parts of ammonia, a semi-solid mass results. This mass, diluted with water, and thrown upon a moistened filter, affords a clear yellow filtrate mixed with a few oily globules, which, however, on refiltration, are completely separated. The oily liquid retained by the filter is now to be well washed with water, which dissolves the amyloxanthate of ammonia, leaving behind the xanthamylamide with the sulphur. This mixture, which has completely separated from amyloxanthate of ammonia, is freed as much as possible from water, and passed through a dry filter, which retains the sulphur. A transparent, pale-yellow oily liquid, is now obtained, which, for the purpose of desiccation, is placed *in vacuo* over sulphuric acid for some time, and, finally, a current of dry carbonic acid gas is passed through the liquid, a gentle heat being at the same time applied.

The xanthamylamide, thus prepared, was analysed. The numbers obtained were, however, only approximative, because the substance could not be freed entirely from impurities, the method of preparing, not excluding small quantities of fusel-oil, and even water, purification by distillation being impossible, because the compound is decomposed under the influence of heat. The substance was analysed in the ordinary manner with chromate of lead, a binoxide of lead tube being used between the chloride of calcium tube and the potash bulbs, to retain any sulphurous acid. The sulphur was determined by ignition in a combustion tube, with a mixture of carbonate of soda, nitrate of potash, and chlorate of potash.

The following results were obtained :

I. 0·1920 grm. of substance yielded :
  0·3460 „ „ carbonic acid,
  0·1781 „ „ water.

II. 0·2290 grm. of substance gave:
    0·4150 „ „ carbonic acid,
    0·2025 „ „ water.
III. 0·2520 „ „ substance gave:
    0·3889 „ „ sulphate of baryta.
IV. 0·2825 „ „ substance gave:
    0·4259 „ „ sulphate of baryta.

These numbers lead to the following percentages:

	I.	II.	III.	IV.
Carbon .	49·11	49·38	—	—
Hydrogen	10·27	9·82	—	—
Sulphur .	—	—	21·15	20·67

The formula

$$C_{12} H_{13} NO_2 S_2$$
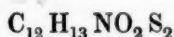
constructed from analogy, requires the following values:

			Theory.		Mean of Experiments.
12 eqs.	Carbon . .	72	.	48·98	49·24
13 „	Hydrogen .	13	.	8·85	10·04
1 „	Nitrogen .	14	.	9·52	—
2 „	Oxygen . .	16	.	10·88	—
2 „	Sulphur . .	32	.	21·77	20·91
		147		100·00	

All my attempts to distil this compound, without at the same time decomposing it, failed. When the temperature rose to 184° C. the liquid boiled, oily drops distilled over, and a strong smell of amyl-mercaptan was noticed. The distillate, dissolved in alcohol, gave a copious white precipitate with protochloride of mercury. The dark-grey residue in the retort, boiled with water and filtered, afforded a liquid which, evaporated to a small bulk, and stirred rapidly, deposited, when cold, an adherent, granular, fawn-coloured precipitate of cyanuric acid. A small quantity, dried and heated in a tube, emitted the peculiar suffocating vapour of cyanic acid. This change is represented by the following equation:

$$3 \underbrace{(C_{12} H_{13} NO_2 S_2)}_{\text{Xanthamylamide.}} = 3 \underbrace{(C_{10} H_{11} S . HS)}_{\text{Amyl-mercaptan.}} + \underbrace{H_3 . C_6 N_3 O_6}_{\text{Hydr Cyanuric acid.}}$$
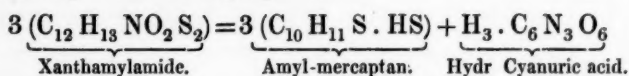
When heat is applied to a quantity of the amide on platinum foil, it emits copious white fumes, and burns with a luminous yellow flame.

Xanthamylamide is insoluble in water, but very soluble in alcohol and ether. It is neutral to test-paper. It is decomposed, when boiled with *hydrate of baryta*; an oily liquid, having the odour of fusel-oil, distils over; ammonia is disengaged at the same time; and the barytic mixture yields with hydrochloric acid and sesquichloride of iron a deep red liquid, indicating the presence of a sulphocyanide.

$$C_{12}H_{13}NO_2S_2 + BaO.HO = C_{10}H_{12}O_2 + Ba.C_2NS_2 + 2HO$$

$$\underbrace{\qquad}_{\text{Xanthamylamide.}} \qquad \underbrace{\qquad}_{\text{Fusel-oil.}}$$
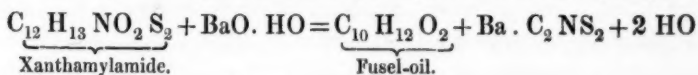
The same reaction takes place with *potash*. *Sulphuric* acid in the cold dissolves it, but on dilution, the mixture becomes turbid from separation of oily particles. When heat is applied, sulphurous acid is evolved, and carbonization ensues. Fuming *nitric acid* acts violently upon it, with copious evolution of red fumes; the resulting solution is rendered turbid by dilution, and oily globules rise to the top. Concentrated *hydrochloric acid* does not appear to act upon it, even on boiling. *Chlorine-water*, however, immediately attacks it, giving rise to a volatile oily liquid; sulphur is at the same time deposited. *Iodine* merely dissolves in xanthamylamide, in the cold, forming a red liquid, which, however, on the application of heat, is quickly decolorised, and a colourless oil, soluble in alcohol, separates. *Bromine* is immediately decolorised by xanthamylamide, a white solid mass resulting, which furnishes, with alcohol, a milky liquid; water now eliminates a colourless oil.

Alcoholic solutions of *acetate of lead, chloride of copper,* and *nitrate of silver* are not precipitated by an alcoholic solution of xanthamylamide. An aqueous solution of *bichloride of platinum* however, furnishes a copious yellow precipitate, having a faint, peculiar odour, and slightly soluble in alcohol, which deposits, on evaporation, a yellow crystalline compound. The mother-liquid from these crystals quickly becomes brown, and, on evaporation, leaves an amorphous brown residue, copious fumes of hydrochloric acid being evolved at the same time. When an alcoholic solution of bichloride of platinum is employed instead of an aqueous one, perfect solution of the substance results, and, on evaporation, a red crystalline compound is deposited. From the filtrate, a definite substance can no longer be obtained. Neither potash nor hydrochloric acid appears to affect this platinum-compound.

Xanthamylamide forms a perfectly definite compound with *protochloride of mercury*. When a drop or two of an alcoholic solution of this salt is added to an alcoholic solution of the amide, merely a faint turbidness occurs; on increasing the proportion of the former,

however, until it is present in considerable excess, a copious white precipitate falls, consisting of minute feathery crystals of the mercury-compound; and this, when washed with cold alcohol, in which it is scarcely soluble, and dissolved in a large quantity of boiling alcohol, deposits the substance, on cooling, in a pure state. The pure compound thus obtained was analysed. The carbon was determined by combustion with chromate of lead, the binoxide of lead tube being employed in Experiment III.; in the same experiment the mercury was determined together with the carbon and hydrogen. The mercury was estimated in the other two experiments by decomposing the substance with a mixture of quick-lime and dry carbonate of soda in a current of carbonic acid, and collecting the mercury in a receptacle formed of the anterior part of the combustion tube. In Experiment V. this operation was combined with the German process for the determination of nitrogen.

I. 0·3865 grm. of mercury-compound, dried *in vacuo*, gave :
    0·1565 „ „ carbonic acid, and
    0·0675 „ „ water.
II. 0·4132 „ „ mercury-compound gave :
    0·1615 „ „ carbonic acid, and
    0·0820 „ „ water.
III. 0·3898 „ „ mercury-compound gave :
    0·1448 „ „ carbonic acid,
    0·0720 „ „ water, and
    0·2250 „ „ mercury.
IV. 0·3645 „ „ mercury-compound, dried in a water-bath, afforded :
    0·7970 „ „ mercury.
V. 0·7150 „ „ mercury-compound yielded :
    0·4160 „ „ mercury, and
    0·1700 „ „ bichloride of platinum and ammonium.

From these numbers the following percentages are deduced :

	I.	II.	III.	IV.	V.
Carbon . .	11·02	10·65	10·13	—	—
Hydrogen .	1·94	2·20	2·05	—	—
Nitrogen . .	—	—	—	—	1·48
Mercury . .	—	—	57·72	58·40	58·18

The simplest atomic expression of these percentages is the formula :

$$C_{12} H_{13} NO_2 S_2 + 4 Hg Cl,$$
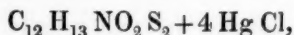
which require the following values :

			Theory.		Mean of Experiments.
12	eqs.	Carbon . .	72·00	10·45	10·60
13	,,	Hydrogen .	13·00	1·89	2·06
1	,,	Nitrogen .	14·00	2·03	1·48
2	,,	Oxygen . .	16·00	2·32	—
2	,,	Sulphur .	32·00	4·64	—
4	,,	Mercury. .	400·28	58·07	58·06
4	,,	Chlorine .	142·00	20·60	—
			689·28	100·00	

This mercury-compound is insoluble in water; it gradually decomposes, however, if kept for a considerable period in contact with it, an odour of fusel-oil becoming perceptible. It is but slightly soluble in either cold alcohol or ether; its solubility, however, is increased on boiling. Cold concentrated sulphuric acid causes an immediate evolution of hydrochloric acid, and elevation of temperature, attended with blackening. Nitric acid acts with energy upon it. Cold hydrochloric acid has no effect upon it; but, on boiling, a portion of the chloride of mercury is dissolved out, and another mercury-compound formed, containing a smaller amount of the chloride than the original compound; it is a white, soft, solid substance, adhering with great tenacity to the sides of the vessels, and, when heated, melts into a white, opaque oil.

On boiling the mercury-compound with potash, a black precipitate is obtained, and an odour of fusel-oil becomes perceptible. Concentrated ammonia, in the cold, immediately decomposes it, with formation of black protosulphide of mercury. Baryta likewise decomposes it on boiling, with evolution of an aromatic volatile compound, protosulphide of mercury remaining behind.

An attempt was made to prepare a quantity of pure xanthamyl-amide by decomposing the mercury-compound with hydrosulphuric acid, but it proved a failure—an oily liquid being obtained, which obstinately retained the hydrochloric acid generated in the reaction; no indication of crystallization was observed. The compound separated is, however, doubtless xanthamylamide.

The analysis of the oily product produced by the action of ammonia upon binoxysulphocarbonate of amyl, its products of decomposition, and the examination of the mercury-compound which I have just now described, establish beyond any doubt the existence in the amyl-series of a substance homologous with the xanthamide of the ethyl-

series. The formation of this body is represented by the following equation :

$$2 (\underbrace{C_{10} H_{11}, 2 CS_2 O}_{\substack{\text{Binoxysulphocarbonate} \\ \text{of amyl.}}}) + 2 H_3 N = \underbrace{C_{12} H_{13} NO_2 S_2}_{\text{Xanthamylamide.}} +$$

$$\underbrace{H_4 N.C_{10} H_{11}, 2 CS_2 O}_{\text{Amyloxanthate of ammonia.}} + 2 S.$$
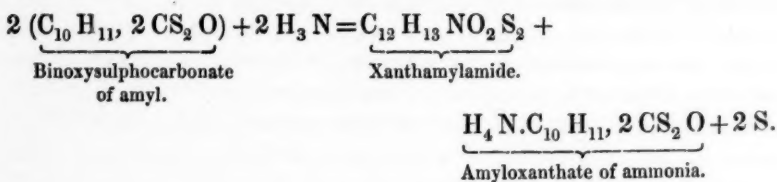
It now remains only to prove, by direct experiment, that the salt produced, together with xanthamylamide, is actually amyloxanthate of ammonia. This salt crystallises from an alcoholic or ethereal solution, in long colourless prisms, which, when cautiously heated between two watch-glasses, give a beautifully crystallised sublimate. It is gradually decomposed by water ; a cold aqueous solution, however, may be obtained, which will deposit prismatic crystals on evaporation *in vacuo ;* but the presence of a large quantity of water invariably gives rise to an oily liquid—a product of decomposition. When evaporated in the water-bath, the salt volatilises with the vapour of water. Exposure to air decomposes this salt even when dry, one of the products of decomposition being invariably sulphocyanide of ammonium. The yellow oil which separates at the same time, on being washed with water and dissolved in alcohol, does not afford a crystalline compound with bichloride of platinum, which suffices to distinguish this substance from xanthamylamide.

An attempt to purify the salt by gently heating it in a current of dry air, with a view to sublimation, proved fruitless; it rapidly decomposed ; white fumes appeared, which condensed to colourless and yellow globules ; the yellow colour of the salt deepened in tint ; when, suddenly, brisk chemical action was set up in the mass, attended by copious effervescence, and the whole changed at once into a turbid yellow fluid, a strong evolution of sulphide of ammonium vapour accompanying the reaction. On dissolving the mass in water, a solution containing sulphocyanide of ammonium was obtained, on which drops of fusel-oil floated.

Caustic potash added to an aqueous solution of the salt under examination, causes the evolution of ammonia, even in the cold, and copiously when heated. Hydrochloric acid separates from it a volatile oily acid of a suffocating odour and insoluble in water. Nitrate of silver gives a yellow curdy precipitate ; acetate of lead, an adhesive, yellow, semi-solid salt, which gradually decomposes and becomes brown. These observations are sufficient to characterize

amyloxanthate of ammonia in an unmistakable manner; nevertheless I thought it desirable to fix, by a number, the formation of this salt, in the decomposition which binoxysulphocarbonate of amyl suffers under the influence of ammonia; and, as amyloxanthate of ammonia could not be obtained sufficiently pure for direct estimation, I selected the lead-salt for analysis.   To prepare this compound, a concentrated aqueous solution of the ammonia-salt was mixed with a large quantity of alcohol, and added to an alcoholic solution of acetate of lead until a precipitate began to appear; alcohol in excess then afforded a clear solution, which, on spontaneous evaporation, deposited delicate shining plates of amyloxanthate of lead, which were washed with alcohol, dried, and submitted to analysis :

> 0·2790 grm. of the lead-compound gave
> 0·1565   „   „ sulphate of lead,

corresponding to

> 38·32 per cent of lead.

Amyloxanthate of lead :

$$Pb.C_{10}H_{11}.2CS_2O$$
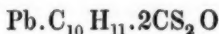
requires

> 38·85 per cent of lead.

On dissolving amyloxanthate of potash, prepared by the ordinary process in alcohol, and adding an alcoholic solution of acetate of lead, a salt was obtained having all the properties of the above compound.   Incidentally to the preceding investigation, a few experiments were made with the acid separated by sulphuretted hydrogen from the amyloxanthate of lead.   This salt, freshly made, was quickly washed with cold water, suspended in alcohol, and treated with hydrosulphuric acid gas; and the colourless liquid separated by the filter from the sulphide of lead was warmed until the free sulphuretted hydrogen was dissipated.   It then possessed an acid reaction, which chloride of barium showed was not owing to sulphuric acid, as it gave no precipitate.   It gave a yellowish-white crystalline precipitate, however, with an alcoholic solution of acetate of lead, and potash gave rise to the crystalline potash-salt.   Evaporation left a liquid highly acid to test-paper, and farther evaporation caused the evolution of white suffocating fumes.

According to a statement of M. Chancel,* the distillation of a mixture of xanthate of potash and sulphomethylate of potash gives
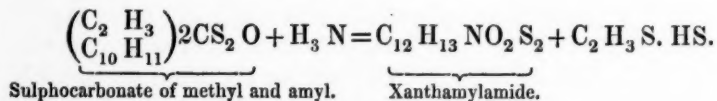
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* Comptes Rendus, April 21st, 1851.

rise to a compound which he terms sulphocarbonate of ethyl and methyl, and which, under the influence of ammonia, is converted into semi-sulphuretted urethane, or xanthamide, and methyl-mercaptan. This statement induced me to institute a few experiments with a view to procure xanthamylamide by analogous means. For this purpose, I prepared the sulphocarbonate of amyl and ethyl, by distilling a mixture of amyloxanthate of potash and sulphovinate of potash:

$$(K. C_{10}H_{11}.2CS_2O) + (C_4H_5.K.2SO_4) = \begin{pmatrix} C_{10}H_{11}.CS_2O \\ C_4H_5.CS_2O \end{pmatrix} + 2K SO_4.$$

$\underbrace{\hphantom{(K. C_{10}H_{11}.2CS_2O)}}$ $\underbrace{\hphantom{(C_4H_5.K.2SO_4)}}$ $\underbrace{\hphantom{\begin{pmatrix} C_{10}H_{11}.CS_2O \end{pmatrix}}}$

Amyloxanthate of potash.   Sulphovinate of potash.   Sulphocarbonate of amyl and ethyl.
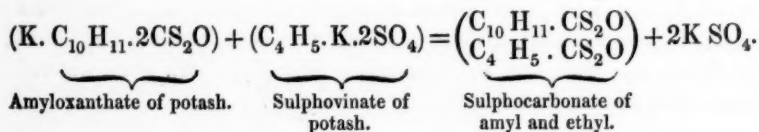
The distillate, which consisted of a yellow aromatic liquid floating above a colourless one, was digested for several days with concentrated ammonia. A yellow-coloured mixture resulted, which emitted the odour of amyl-mercaptan. I was, however, unable to obtain positive proof of the formation of xanthamylamide. I was more fortunate with regard to the analogous sulphocarbonate of methyl and amyl. This compound, when heated with dry ammoniacal gas, and digested with it for several months, gave rise to a substance which possessed all the properties of xanthamylamide; the quantity obtained, however, was too small to admit of an analysis.

The formation of xanthamylamide in this reaction is represented by the equation:

$$\begin{pmatrix} C_2H_3 \\ C_{10}H_{11} \end{pmatrix} 2CS_2 O + H_3 N = C_{12}H_{13}NO_2 S_2 + C_2H_3 S. HS.$$

$\underbrace{\hphantom{\begin{pmatrix} C_2H_3 \\ C_{10}H_{11} \end{pmatrix} 2CS_2 O}}$ $\underbrace{\hphantom{C_{12}H_{13}NO_2 S_2}}$

Sulphocarbonate of methyl and amyl.   Xanthamylamide.

I cannot conclude without publicly acknowledging the kind advice and assistance of Dr. Hofmann during the prosecution of this investigation.

XV.—*On a New Process for the Detection of Fluorine when accompanied by Silica.*

By George Wilson, M.D.

Having had occasion recently to examine several substances containing a small amount of fluorine, along with a large amount of silica, I have put in practice two processes, one of which is so easily managed, and has yielded such excellent results, that I bring it before the attention of the members of the Chemical Society.

The substances which I had to examine were the ashes of straw, hay, coal, and charcoal; and likewise granite, basalt, greenstone, and clinkstone, in the majority of which, fluorine has not hitherto been detected, nor, indeed, sought for, owing, doubtless, to the practical difficulties which attend the detection of fluorine when accompanied by much silica. The chief difficulty in such inquiries arises from the necessity of carrying on the analysis in vessels of platinum, which makes it impossible to subject large quantities of material to investigation.

The following process meets this difficulty, as it requires only the ordinary glass and porcelain vessels of the laboratory, and may be prosecuted with any amount of material. It is founded upon the very familiar fact, that when a fluoride, combined or mixed with silica, is heated with oil of vitriol, the fluorine and silicon are evolved in combination, as the well-known fluoride of silicon (SiF_3); and it is applicable to all silicated fluorides which yield this gas. It is further applicable to compounds containing mere traces of fluorides, but free from silica, which are brought within the compass of the process, by the deliberate addition of silica to them, so as to admit of their being heated in large quantity with oil of vitriol in glass vessels. In either case, the fluoride of silicon set free is conveyed by a bent tube from a flask or retort into water. The resulting solution, containing some gelatinous silica, is supersaturated with ammonia, and evaporated to dryness, during which process the fluoride of silicon and ammonium ($2\,SiF_3 + 3\,NH_4\,F$) is resolved into silica, which is rendered insoluble, and fluoride of ammonium, which is dissolved by digesting water on the evaporated residue. The solution of the ammonio-fluoride is then evaporated to dryness, and heated with oil of vitriol, in a platinum crucible, covered by a piece of waxed glass, having lines traced through it, so as to permit the hydrofluoric acid evolved to etch the glass. I have tried this process

with Peterhead and Aberdeen granite, with basalt from Arthur's
Seat, greenstone from Corstorphine Hill, and clinkstone from Black-
ford Hill—all three in the neighbourhood of Edinburgh.   I have
also tried it with the ashes of barley-straw, of hay, of coal, and of
charcoal; and in addition with a fossil bone, containing much car-
bonate of lime, and with a deposit from the boiler of an ocean
steamer.   To the bone and to the boiler deposit, pounded glass was
first added.   I lay before the Society some of the specimens obtained
in this way.   They are not selected successful ones, but represent
the earliest trials.   Where the rocks under examination have been
weathered, or the substances (such as plant-ashes) have contained
salts of volatile acids (for example, chlorides and carbonates), I have
treated them first with oil of vitriol in the cold, so as to evolve
hydrochloric acid and carbonic acid.   On afterwards raising the
liquid to the boiling-point, in a flask with a bent tube, a gas was
given off, if fluorine were present, which deposited gelatinous silica
when passed through water, and produced with it a solution which
gave a gelatinous precipitate with potash.   The whole of the fluoride
of silicon is given off as soon as the oil of vitriol has reached its
boiling-point.   I am at present engaged in applying this process to
a variety of substances, and in ascertaining its applicability to the
quantitative determination of fluorine.   I forbear, in the meanwhile,
to enlarge upon the interesting geological, mineralogical, and physio-
logical results which may be expected to flow from the discovery of
fluorine in trap rocks, and the recognition of its comparative abun-
dance in plants.

PROCEEDINGS

MEETINGS OF THE CHEMICAL SOCIETY.

Anniversary Meeting, March 30, 1352.

Professor DAUBENY, President, in the Chair.

The following Annual Report was read by the President.

Gentlemen,

The Twelfth Anniversary of this Society, which we are to-day assembled to celebrate, opens under circumstances peculiarly auspicious, suggesting to us matter for congratulation as to the past, and for encouragement with respect to the future.

Our body has already, by the number of its members, by the value of its contributions to science, and by the increasing interest testified in its proceedings, vindicated to itself a full claim to the place which, under the presidentship of Mr. Brande, it had acquired amongst the chartered scientific societies of the metropolis; and is now, moreover, I am happy to add, established in a locality more worthy of its high position, and capable of affording those accommodations for the reception of its members and for the display of its library and of its collections, of which it has long felt the want.

The advantages of the present abode need not indeed be particularized in addressing members, upon the recollections of most of whom the deficiencies of our former locality must be vividly impressed; nor could they have been secured at a more fortunate moment than the present, when they enabled us to accommodate that large assemblage of chemical products which were so liberally contributed by various individuals at the close of the Great Exhibition of last year.

In consequence of these donations, we may indeed flatter ourselves

that the Chemical Society will hereafter be resorted to, not only as the spot where the newest discoveries in this department of science may be expected to be announced, and the most authentic information on the existing state of our knowledge on such subjects obtained; but also as the depository of all that is curious and important amongst the natural or artificial productions, which may from time to time be elaborated through the instrumentality of chemical processes. And when we recollect how difficult and how toilsome, even in expert hands, the preparation of many of these compounds is found to be, how little there is to induce the mere manufacturing chemist to exercise his skill upon them, and how unprofitable it would be for the most assiduous cultivator of the science to obtain by his own unassisted labours any considerable number of the multifarious combinations which art is capable of bringing about between the elements of matter, the utility of such a depôt for the reception of such presents, as we are now attempting to form, cannot perhaps be too highly appreciated.

Each of the substances, indeed, stored up within our cases, may be regarded as a standard with which to compare any new body lighted upon in the progress of chemical investigation, and thus as not only aiding directly in the advancement of science, but also in the prevention of much unnecessary labour, by pointing out what has already been ascertained in each department of inquiry. I may, therefore, take upon myself to congratulate the Society most warmly on the progress that has been made towards the formation of a Chemical Museum, and to point out as one of the incidental benefits flowing from the Great Exhibition of last year, that it has been the means of affording such ample contributions to that treasury of scientific products, which it is our pride to possess.

I should, indeed, have deemed the acquisition of a place in which these advantages might be secured, as a worthy object upon which to expend a portion of our reserved funds, had the general interests of science alone been consulted in this appropriation of them; but there was also reason to hope that every addition to our means of imparting knowledge would be followed by a greater disposition on the part of the public to avail itself of them; and hence that these increased facilities would be followed by a proportionate augmentation in the number of our members. And although the influence of these changes will be more felt hereafter, yet I am happy to report that already the increase which has taken place in our members, is such as to show that this anticipated result has, to a certain extent, been realised.

It appears, from the Secretary's Report, that there have been elected since the last Anniversary Meeting, 24 members, whilst the deaths and resignations together amount only to 8; showing an increase over last year of 16, from which number, however, might perhaps be deducted 2, who have suffered the time to expire within which the payment of the entrance-fee should have been made, and whose election is consequently void.

According to this calculation, the actual number of Fellows will be 243; whereas, at the last Anniversary Meeting, it was only 229, showing that the steady though slow increase in our number, which had been remarked on former anniversaries, still continues.

STATEMENT OF THE NUMBER OF FELLOWS OF THE CHEMICAL SOCIETY AT THE PRESENT TIME, AND AT THE CORRESPONDING PERIOD OF LAST YEAR.

Present number of Fellows 245
Elected since last Anniversary Meeting . . . 24
Deaths and resignations since last Anniversary Meeting . 8
Increase since last Anniversary Meeting . . . 16
Number of Fellows at period of last Anniversary Meeting 229

T. Redwood,
Secretary.

March 22, 1852.

The three Fellows whom we have lost by death since our last Anniversary, are Mr. Richard Phillips, Mr. William West, and Mr. Henry Beaufoy.

The first of these gentlemen had vacated the office in this Society in which I had the honour to succeed him, only a short time, when he was seized by an attack of bronchitis, which quickly terminated an useful and busy life, mainly dedicated to the investigation of physical truth.

Mr. Richard Phillips and his elder brother William, who died several years ago, were the sons of a printer, in George Yard, Lombard Street, a member of the Society of Friends.

The elder brother was distinguished as a crystallographer and as a mineralogist, in which capacities, as well as by his compilations in geology, he aided materially the early progress of that science. The

younger, educated as a druggist, under the late Mr. William Allen, of Plough Court, became at least equally distinguished for his acquirements in Chemistry.

His reputation, indeed, in this line, secured to him at an early age the honour of a place in the Royal Society, and caused him also to be elected as an honorary member of the Medico-Chirurgical Society, thus bringing him into intimate connexion, on the one hand, with the chemical philosophers, and on the other, with the physiologists and physicians of the age.

He might indeed be regarded, during the latter part of his life, as a connecting link between the chemists of the last generation and of the present, having been the contemporary of Davy and Wollaston, no less than of Faraday and Graham; and in his death we have lost one of the last of that distinguished band of philosophers, who, before chemical science had so enlarged its boundaries, as to include within its domain and to comprehend within the operation of its laws the products of animal and of vegetable life, occupied themselves almost exclusively in the investigation of the combinations of which mineral bodies are susceptible.

Mr. Phillips' labours in this latter department were characterized by great neatness and precision; so that they may indeed be appealed to at the present time as models of skilful and exact research. To him we are indebted for the first correct analyses of the Bath waters, in the course of which investigation he discovered the cause of the apparent uncertainty in the indications afforded by the common tests for iron, caused by the variations that occur in their effects, according as carbonate of lime is present or not.

This was followed by an examination of other celebrated mineral springs, and by that of several rare minerals, one of which relates to his discovery of phosphoric acid combined with uranium,* a fact which had escaped the searching eyes of Berzelius, who was thus as much outdone in the above particular by the subject of this notice, as Davy had been by him when he detected the presence of phosphoric acid in Wavellite, which the great English chemist had overlooked.

By this and other of his contributions to science, Mr. Phillips so raised his reputation, that he was pronounced by Dr. Thomas Thomson, in his Chemistry, the first of modern analytical chemists.

It was, however, in the pharmaceutical branch of the subject that his services were most conspicuous, as might be expected from one of his acuteness, after a training in the above-mentioned establish-

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* Annals of Philosophy for 1823.

ment in Plough Court, of which the chemical reputation ranked justly so high.

Indeed, the perfect familiarity he possessed with the processes in use, enabled him to detect the errors into which the framers of our London Pharmacopœia had fallen ; whilst the keenness of his reviews gave currency to his censures, of which even those who smarted under their severity, could scarcely help acknowledging the justice. Accordingly, at a subsequent period, he was especially consulted on the drawing up of two of the editions of the London Pharmacopœia by the College of Physicians itself, whose previous labours in that department he had so severely criticised, and thus led the way to many of the much needed corrections in the processes since introduced.

Indeed, during the latter part of his life, he was appealed to as perhaps the highest living authority in this branch of chemistry ; and his translation of the London Pharmacopœia, the last edition of which he was engaged at the time of his death in superintending, was looked upon as the best book of reference on all chemical questions involved in the preparation of medicines.

From the year 1821, Mr. Phillips conducted the Annals of Philosophy ; and when that periodical was incorporated with the London, Edinburgh and Dublin Philosophical Magazine, his services were secured as one of its editors, a post he held till his death.

For this office he was well qualified, from the frankness and friendliness of his character, no less than from his acuteness of intellect, which enabled him to subject the scientific communications which came before him to that rigid scrutiny, which the promulgator of every new view and original fact must be prepared to encounter, before either the one or the other receives the stamp of public recognition, and can be admitted as a part of the common patrimony of science.

Mr. Phillips was successively Lecturer on Chemistry at the London Hospital ; at the Government Military College, at Sandhurst ; at Mr. Grainger's School of Medicine, in Southwark ; and at St. Thomas's Hospital.   In 1839, he was appointed Curator of the Museum of Practical Geology, now in Jermyn Street, an office which he continued to hold till the date of its formal opening, under the auspices of H.R.H. Prince Albert, in July last, on the very day before which, he breathed his last, at the age of seventy-two, after a short illness.

Although I was not myself fortunate enough to be frequently thrown into his society, I had seen enough of him to be persuaded of

the truth of the character given of him by his intimates, who describe him as not less remarkable for his ready power of repartee, and keen sense of the ridiculous, than for the quickness of observation, range of knowledge and precision of intellect, by which he was publicly distinguished.

Mr. William West was born at Wandsworth, in the year 1793, of parents, both of whom were members of the Society of Friends.

In the year 1816, he established himself as a druggist, at Leeds, where he became quickly distinguished by his exemplary diligence and unremitting attention to the scientific as well as to the commercial part of his business.

His spare moments were mostly occupied in the study of the most recent discoveries in chemistry, in analytical researches, and in the preparation of the various papers which he contributed to different scientific societies. Of these, no less than twenty-three may be enumerated which were read before the Leeds Philosophical and Literary Society; and these were not only of a kind connected with his own professional pursuits, but also related to various other departments of science and literature. He took an active and prominent part in the foundation of the above-named society, of which he became successively the Honorary Secretary, the Vice-President, and the President.

He also interested himself warmly in the Leeds Mechanics' Institute, and was Vice-President of the Geological and Polytechnic Society of the West Riding of Yorkshire, to which he contributed various papers. On the 1st of March, 1842, he was elected an Associate of the Institute of Civil Engineers, and was awarded the Telford Medal, on the 9th of December, 1846, for a paper " On Water for Locomotive Engines." He was also elected a Fellow of the Royal Society, on the 19th of February, 1846. Mr. West was Chemical Lecturer to the Leeds School of Medicine, from the year 1831 to 1846, when ill-health compelled him to resign this post, as from the same cause he soon after did the commercial part of his business, though still continuing to be engaged in analyses and in scientific investigations of a judicial kind, in which his authority was much esteemed, up to the period of his decease, which took place on the 10th of September, of last year.

My own acquaintance with Mr. West dates as far back as the period, when he formed with myself one of that little band of promoters or cultivators of science, who, obedient to the summons of Sir David Brewster, assembled at York, in the year 1831, and

whilst there, in spite of the smallness of our numbers (which, however, besides the illustrious philosopher who first projected the Meeting, included the names of Dalton, of Murchison, of Forbes, and of Sowerby), had the boldness to organise the scheme of that great scientific association, which next year obtained its full development at Oxford, and has since been welcomed in almost every large city of the British dominions.

The last time I saw Mr. West, was at the meeting of this same body, which took place last year at Ipswich, when he exerted himself to persuade the General Committee to fix upon his native town for their place of meeting in the year 1854, although, with a consciousness of declining health, which the event has shown to have been but too well founded, he declared his persuasion that he should not be alive at the time to welcome us himself.

The late Mr. Henry Beaufoy, of South Lambeth, passed his time in such complete seclusion from the routine of society, that there are very few particulars to relate respecting him.

He was educated for many years under Dr. Goodenough, at Ealing School, which well accounted for his classical attainments and the literary predilections he preserved throughout life.   When, however, on the death of his elder uncle, it was considered necessary by the family that he should become a mercantile man, Henry Beaufoy, under the guidance of Mr. Nicholson of Soho Square, gave his attention to practical chemistry, which eventually enabled him to conduct with success a large manufactory, by causing him to appreciate and adopt some modern improvements in science, of great value to his trade.

Deeply grateful as he was to that Providence which had bestowed on himself and all his father's children so many blessings, he considered it an act of duty to prove his gratitude while living, by appropriating a large portion of his income to charitable purposes. Of the extent of these acts of munificence, the following statement may convey a brief, although a very inadequate representation.   To the City of London School alone, he appears to have been a benefactor to the amount of £10,000.   Then he had established four scholarships for four students, at Cambridge, and had instituted various prizes for the best essays, and for other purposes.   Amongst the rest was £1,000 to encourage the study of Shakspeare, the interest to be given away to the most deserving candidate upon the anniversary of the poet's birthday, which chanced to coincide with his own.

Mr. Henry Beaufoy was the eldest son of Colonel March

Beaufoy, well known for his elaborate nautical and hydraulic experiments, the results of some of which, the subject of this notice published in a handsome quarto volume. The entire impression of this work, comprising I believe no less than fifteen hundred copies, he, with his accustomed liberality, distributed gratuitously amongst scientific men and societies, thus performing at once a public service and an act of filial duty.

He was born on the 22nd of April, 1786, died on the 12th of July, 1851, and lies buried in Norwood Cemetery, in the same grave with his wife, as a monument to whom, he had erected, at his own expense, at Lambeth, a very handsome building for a ragged school, which he established and endowed most liberally.

The Papers that have been read at our Meetings since the last Anniversary are by no means inferior either in number or in interest to those of preceding years. I shall not pretend, however, to do more than just to present to you a list of their titles, which are as follows:

Papers read at the Meetings of the Chemical Society, from April 7th, 1851, to March 15th, 1852, inclusive.

" On the Composition of the Water of the Dee and the Don at Aberdeen, with an investigation into the action of Dee-water on lead pipes and cisterns." By John Smith, M.D., Fordyce Lecturer on Agriculture, and Assistant in the Chemical Laboratory of Marischal College.

" On a peculiar property of Ether and some Essential Oils." By Dr. C. F. Schönbein.

"On the Analysis of the Sediment deposited from the River Nile, in Lower Egypt." By Matthew W. Johnson.

" Notice of a Specimen of Chlorobromide of Silver, from Chili." By Colonel Philip Yorke.

" On the Tests for Nitrates, and a New Test for Nitrites." By David S. Price, Ph. D.

" On a New Test for Iodides." By the same.

" Analysis of Milk." By John Ellis Roberts.

" Observations on the Teas of Commerce." By Robert Warington.

" On the Composition and Properties of the Carbonates of Lead, constituting the White Lead of Commerce." By J. A. Phillips.

" On the Equivalent of Phosphorus." By Professor Schrötter.

"Note on a case of. Leakage in a Leaden Water-cistern." By J. H. Gilbert, Ph. D.

"On Dibenzoylimide, a new derivative of Oil of Bitter Almonds." By Joshua H. Robson.

"On Chromic Acid and Sesquioxide of Manganese." By J. Adam Fairie.

"On the Chromate of Ammonia." By the same.

"On Etherification." By Professor Williamson.

"On the Valuation and Composition of Protochloride of Tin." By Professor Penny.

"On the Chemical Examination of the Metals and Alloys known to the Ancients." By J. Arthur Phillips.

"Observations on the Phenomena of Animal Phosphorescence." By Thornton J. Herapath.

"Analysis of a Mineral containing Gold, from the province of Coquimbo. Chili." By F. Field.

"Description of Lapis Lazuli, found in large quantities in the Cordilleras of the Andes." By the same.

"On the Spontaneous Decomposition of Gun-cotton and its congeners." By J. H. Gladstone, Ph. D.

"On the Action of Arsenious Acid on Albumen." By John B. Edwards.

"On the Action of Ammonia on Sebacic Ether." By T. H. Rowney.

"Analysis of the Water supplied by the Bristol Water-works Company." By Thornton J. Herapath.

"On a quick approximative method of estimating minute quantities of Iron by means of a Colorimeter." By the same.

"On the Decomposition of Citrate of Lime in contact with putrifying Curd." By Henry How.

"On a new method of obtaining Hippuric Acid in considerable quantity without evaporating the urine, and on some of its products of decomposition." By Edward Riley.

"On Populin." By M. Rafaelle Piria.

"On the variation in the relative proportion of Potash and Soda present in certain samples of Barley grown in plots of ground, artificially impregnated with one or other of these alkalies." By Professor Daubeny, F.R.S.

"On the Compounds of Cotton with the Alkalies." By J. H. Gladstone, Ph. D.

"On the Occurrence of Capric and Caprylic Acids in some Fousel Oils." By T. H. Rowney.

" On Dr. Keller's supposed formation of Metacetonic Acid from Flour and Leather." By-R. W. Forster.

" On the detection of Alum in Flour, with remarks on the preparation of Distilled Water and pure Potash." By J. H. Pepper.

" Contributions towards the history of Tannic Acid." By Dr. Strecker.

Besides these Memoirs, formally communicated to the Society, we have had at various times laid before us interesting notices of researches now in progress in foreign countries; as, for instance, of the new process for determining urea, invented by Baron Liebig, which promises, when fully worked out, to facilitate greatly the observations which the physician and the physiologist are equally interested in making, respecting the changes that occur in this important ingredient of the urinary secretion.

And now, Gentlemen, little more remains, except for me to express my warmest thanks to the Members of the Council generally, and to the Secretaries in particular, for the kind manner in which they have relieved me from the more onerous part of my duties, by the constant attention bestowed by them on the business of the Society, rendered this year more than ever laborious by the arrangements consequent upon the change of our rooms. Without their advice and co-operation, indeed, it would have been impossible for me, living as I do at a distance from the metropolis, to have accepted the honourable post you have in so flattering a manner assigned to me, however desirous I might be to discharge its duties, so far as my time and abilities permitted. Indeed I have more reasons than one to apologize to you for my deficiencies and shortcomings, especially when I compare myself to the distinguished men who have preceded me in this office. Not only have I felt myself less able efficiently to discharge its duties, by reason of my residing so much farther from my post than any of the former presidents, but, divided as my time has long been between two complicated and rapidly advancing sciences, I am necessarily the less competent to grapple with many of those intricate questions in chemical philosophy upon which I might be expected to offer an opinion.

Perhaps, indeed, paradoxical as it may sound, the wide range of subjects which Chemistry herself embraces, or to which she is able to lend a helping hand, may be regarded as the very circumstance which has most contributed to reconcile me to undertaking other duties in conjunction with those which devolve upon me as Professor of Chemistry in the University to which I belong. The changes,

for example, brought about by nature or induced by art in the growing vegetable, cannot but be influenced by those laws, which are common to matter, whether inert or living, and thus are brought, to a certain extent at least, under the domain of Chemical Philosophy. Hence, Vegetable Physiology (and Rural Economy also, so far as that art is directed by scientific principles) appears less alien to the pursuits of a chemist than it would be to those of a man of science, who was devoted to any kind of natural philosophy more limited in its range of subjects. And, I may add, this infinite variety in the nature of the researches which our science includes within its jurisdiction, affords, in my opinion, the most convincing argument that can be offered on behalf of the necessity for the existence of a society like ours, exclusively dedicated to its promotion. Formerly, indeed, the attempt to draw off from the Philosophical Transactions any portion of that class of contributions upon which so much of their credit has ever rested, might have been viewed with some jealousy by the Royal, the common parent of all those societies which have subsequently started up.

But such a feeling cannot reasonably be entertained at the present moment, when chemistry has so enlarged its boundaries as to embrace within its compass the kingdoms of living as well as of inanimate nature. For without here pronouncing upon the difficult and much debated question as to the extent to which vital functions are influenced by chemical laws, it may be sufficient to establish the justice of my remark, if we recollect that an infinite variety of curious and important chemical products owes its origin to vital processes, in so far as the latter, by bringing together the particles of matter under conditions not imitable by art, do in fact supply us with a number of new principles to work upon, in addition to those furnished by the mineral kingdom ; elements, indeed, inasmuch as they are the roots of new combinations, although themselves compounds, as being made up of bodies regarded by us as simple.

Under such circumstances, it must be apparent to every one that the Royal Society could never have taken cognizance of the whole of that vast range of subjects which modern chemistry embraces, and that many papers of great promise and of much practical utility would have been lost to the world, but for the existence of such a society as our own. Moreover, the experience of the last ten years has completely established the position, that at no period in the history of the Royal Society have more important Chemical Papers appeared in its Transactions, and at none has the number of Communications to it in the same department been so numerous as they

have been since the Chemical Society has been established. I need only allude to the memoirs of Graham, of Hofmann, and of Brodie, in proof of the former part of this assertion, namely, as to the value of the Chemical Papers which have been recently supplied to the Philosophical Transactions by members of the Chemical Society.

With respect to the second part of my statement, I may remark, that the average of papers on chemical subjects, not including electricity, contained in the Philosophical Transactions during the ten years preceding the foundation of the Chemical Society, was only about 3 in two years, or 16 in ten years; that during the first four years of our existence, namely, from 1842 to 1846 inclusive, the number of papers was 12, or $2\frac{1}{2}$ yearly; whilst, during the last quinquennial period, they have risen to 20, or to 5 on the average each year.*

Yet although there is good ground for believing that the establishment of this Society, so far from damaging the interests of the Royal, has rather tended to advance them, serving, as it has, as a feeder to that great original trunk of scientific information; and although it is true, that the spirit of the age no less than the extension of the fields of research in each department, calls imperatively for a multiplication of scientific institutions throughout the country, it affords at the same time no argument against their juxtaposition. Indeed, any arrangement which should effect this object, with respect to the chartered scientific institutions of the capital, would have much to recommend it, not only on the ground of economy and convenience, inasmuch as one set of accounts might then do the work of several societies, and one meeting-house serve the purpose, perhaps, of the whole number so brought together; but also in materially promoting the object which each of us has in

* This may be seen by the following table.

1831	2 Papers.		1842	3 Papers.	
1832	0 „		1843	2 „	
1833	2 „		1844	2 „	
1834	2 „		1845	5 „	
1835	0 „		1846	1 „	13 Papers.
1836	1 „		1847	1 „	
1837	2 „		1848	4 „	
1838	1 „		1849	4 „	
1839	1 „		1850	9 „	
1840	5 „		1851	5 „	23 „
1841	0 „				
Total . . 16			Total . . 36		

common, by facilitating the intercourse between men engaged in different departments of inquiry, and by removing some of the obstacles that impede their mutual co-operation ; thus rendering the same service to the metropolis which the British Association for the Advancement of Science professes to do with reference to the provinces.

Whilst, therefore, I congratulate you, as indeed I have already done, on the additional conveniences afforded by our present suite of apartments over our last, I would still more heartily hail the day which should see all the principal chartered societies of the metropolis under a common roof, pursuing their separate labours indeed independently, but at the same time deriving mutual support and assistance from their contiguity ; exercising no paramount jurisdiction, but moving forwards in harmony and concert, as becomes the federal members of the great republic of science.

The audited Statement of the Treasurer's Account was submitted to the Society as follows :

AUDITED REPORT OF THE TREASURER.

ROBERT PORRETT (TREASURER) IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON.

Dr. side

1851–1852		£	s.	d.
1851 March 31. 1852 March 30.	To Balance from last Account	263	9	0
March 30.	,, Subscriptions £221 2s. and Compositions £30, since received	251	2	0
,,	,, Donation to Library Fund	10	0	0
,,	,, Admission Fees from 22 new Members	44	2	0
,,	,, Two Years' Dividends to 5th Jan. last, on £400, 3 p. c. Consols, minus Property Tax	23	6	0
,,	,, Proceeds of Sale of £100, 3 p. c. Consols, minus Brokerage	98	5	0
,,	,, One Year's Rent in advance, to Jan. 1853, from the Meteorological Society, for use of Rooms	20	0	0
,,	,, Proceeds of Sale of "Memoirs," by Mr. Taylor	4	14	10
		£714	**18**	**10**

Cr. side

1852		£	s.	d.
March 30.	By payment to Mr. Abel, for Translations	9	2	6
,,	,, Ditto to Mr. Watts, One Year's Salary, as Editor of "Journal"	50	0	0
,,	,, Ditto to Mr. Medlock, One Year's Salary, to 31st Dec. last	25	0	0
,,	,, Ditto to ditto, for Petty Cash	8	3	8
,,	,, Ditto to Mr. Redwood, for ditto	6	1	9
,,	,, Ditto to H. Baillière, for Publishing Journals	128	13	9
,,	,, Ditto to ditto, for Periodicals to 30th June last	7	1	6
,,	,, Ditto to Williams and Norgate, for Foreign Books	6	0	6
,,	,, Ditto to John Chapman, for One Year's Rent of Apartments, 142, Strand, to Michaelmas last, £55; and for Tea and Coffee, £8	63	0	0
,,	,, Ditto for a Turkey Carpet for Council-room	11	7	0
,,	,, Ditto to R. Ireland, for Book-cases and Mahogany Seats	52	13	0
,,	,, Ditto to Thos. Ames, for Thirteen Mahogany Chairs	22	15	0
,,	,, Ditto to Thos. Holland, for a Mahogany Glass Case	21	0	0
,,	,, Ditto to S. Gale, for Gas-fittings, Diagram-board, &c.	22	8	0
,,	,, Ditto to J. Crandal, for Bookbinding	7	8	10
,,	,, Ditto to T. Treloar, for Cocoa-nut Matting	2	11	9
,,	,, Ditto to Bunn & Co., for Floorcloth	11	10	0
,,	,, Ditto to Mr. Rickers, for Books	22	2	0
,,	,, Ditto to W. S. Burton, for Coffee-machine and Teaspoons	3	6	0
,,	,, Ditto for Bottles, and expenses in removing Specimens from the Great Exhibition	5	18	0
,,	,, Ditto to Thos. Riddle, for Chairs, &c.	15	18	0
,,	,, Ditto to S. Kirkman, for tea, coffee, &c., including £4. 9s. for Attendance and Table, to 31st Dec. last	7	14	2
,,	,, Ditto to Cavendish Society for Subscription, 1852	1	1	0
,,	,, Ditto for Envelopes and Postage-stamps for Treasurer	0	2	6
,,	,, Ditto for Power of Attorney to receive Dividends	1	5	6
,,	,, Ditto to John Gifford for Engraved Brass Plate	1	14	6
,,	,, Ditto to C. Button, for 246 Stoppered Bottles	9	10	6
,,	,, Ditto to Yool & Son, for Coals and Wood	1	19	6
,,	,, Ditto to Schulze & Co., for Printing Circulars	0	18	6
,,	,, Ditto to Directors of Polytechnic Institution for Rent to 25th inst.	60	0	0
,,	,, Ditto to ditto, for Tables and Furniture	15	18	0
,,	,, Ditto to R. Taylor, for 15 Nos. of "Philosophical Magazine"	1	15	0
,,	,, Ditto to ditto, for Printing Catalogues, &c.	10	0	0
,,	,, Ditto to Collector, for Poundage, including 14s. for Stamps, &c.	10	19	6
,,	,, Balance carried to his Debit in next Account	91	12	2
		£714	**18**	**10**

London, March 30, 1852.

R. PORRETT, Treasurer.

Examined and found correct,

(Signed) { J. DENHAM SMITH, ALFRED WHITE, JOHN THOMAS WAY, } Auditors.

Mr. J. J. Griffin and Dr. Price having been appointed Scrutators, the Meeting proceeded to the Election of Council and Officers for the ensuing year; and the following gentlemen were declared to have been duly elected :

PRESIDENT.

Charles G. B. Daubeny, M.D., F.R.S., F.G.S., F.L.S.

VICE-PRESIDENTS.

William Allen Miller, M.D., F.R.S. Robert Warington, Esq.
Lyon Playfair, C.B., Ph.D., FRS. Colonel Philip Yorke, F.R.S.

TREASURER.

Robert Porrett, F.R.S., F.S.A.

SECRETARIES.

Benjamin Collins Brodie, F.R.S. Theophilus Redwood, Ph.D.

FOREIGN SECRETARY.

A. W. Hofmann, Ph.D., F.RS.

OTHER MEMBERS OF THE COUNCIL.

Thomas Anderson, M.D., Edinburgh. H. Bence Jones, M.D., F.R.S.
John Blyth, M.D., Cork. J. P. Joule, F.R.S.
Dugald Campbell, Esq. G. D. Longstaff, M.D.
Warren De la Rue, Ph.D., F.R.S. J. Arthur Phillips, Esq.
J. H. Gladstone, Ph.D. A. W. Williamson, Ph.D.
Thomas Graham, F.R.S. George Wilson, M.D., F.R.S.

It was moved by Dr. Warren De la Rue, seconded by Dr. Lyon Playfair, and

Resolved,

That it is desirable to alter the By-laws of the Society, in so far as they relate to the number of Vice-Presidents; so that those Fellows of the Society who have served the office of President, shall be annually proposed for election as Vice-Presidents in addition to the Vice-Presidents elected under the present By-laws; and that such alteration be made as follows :

At page 11 of the printed Charter and By-laws of the Society, in the second paragraph, and sixth line from the top, the words "*four Vice-Presidents*" to be changed to "*four or more Vice-Presidents.*"

At page 15, in By-law VII, the last line of this By-law, being the fourteenth line from the top of the page, to be expunged, and the following words to be substituted:—"*Fellows who have filled the office of President at any time since the formation of the Society, shall be proposed by the Council for election as Vice-Presidents; and this proposition shall be renewed every year, excepting when any such are again elected to the Presidency. There shall be four other Vice-Presidents who have not filled the office of President, and every year one of these shall retire from office.*"

The thanks of the Society were voted to the President, Officers, and other Members of Council, for their services during the past year.

April 5, 1852.

Colonel Philip Yorke, Vice-President, in the Chair.

The following donations were announced:

" The Pharmaceutical Journal for April:" from the Editor.
" The Literary Gazette for March 20th and 27th and April 3rd:" from the Publishers.

The following gentlemen were duly elected Fellows of the Society:

The Rev. W. Thomson, M.A., Queen's College, Oxford.
Robert Keates, Esq., 35, Carter Street, Walworth.
Samuel Gale, Esq., 17, Bloomsbury Square.

A paper was read:

" On the Detection and Qualitative Separation of Tin, Antimony, and Arsenic; and on the relation existing between these metals and others which are precipitated from their acid solutions by sulphuretted hydrogen," by Charles L. Bloxam.

April 19, 1852.

PROFESSOR DAUBENY, President, in the Chair.

The following donations were announced :

"Transactions of the Royal Scottish Society," Vol. III, Part 5 : from the Society.

Specimens of :

Caprylic Alcohol : from Dr. Williamson.
Anhydrous Benzoic Acid : from M. Gerhardt.

The following papers were read :

1. "Researches on the Constitution of Organic Acids :" by M. Charles Gerhardt; communicated by Dr. Williamson.
2. "Note on the Preparation of Carbonate of Amyl :" by John A. Bruce.
3. "New Formation of Salicylic Acid :" by H. Gerland. (From a Letter of Dr. Kolbe to Dr. Hofmann.)

May 3, 1852.

ROBERT WARINGTON, ESQ., Vice-President, in the Chair.

John William Perkins, Esq., Union Wharf, Narrow Street, Limehouse, and William Wilson, Esq., 9, Maida Hill, were duly elected Fellows of the Society.

The following papers were read :

1. "On the Preparation of Anhydrous Acetic Acid :" by M. Charles Gerhardt.
2. "Chemical Memoranda :" by Robert Warington.
3. "On the Action of Ammonia upon Binoxysulphocarbonate of Amyl :" by Matthew W. Johnson.
4. "On a New Process for the Detection of Fluorine when accompanied with Silica :" by George Wilson, M.D.

May 17, 1852.

PROFESSOR DAUBENY, President, in the Chair.

Captain James Whitmore, 63, Park Street, Grosvenor Square, was duly elected a Fellow of the Society.

A paper was read :

" On a New Test for Strychnine :" by J. H. Pepper.

The Author suggests the use of a solution of red prussiate of potash in oil of vitriol as a test for strychnine, this substance developing in the solution a violet-blue colour, when added in the dry state, or dissolved in ether.   An aqueous solution cannot be used, as the presence of water alone produces a blue colour.

A verbal communication was made to the Society by Dr. Gladstone, " On the Atomic Weights of some of the Elements."

June 7, 1852.

COLONEL PHILIP YORKE, Vice-President, in the Chair.

The following donations were announced :

" Specimens of Crystallized Lead :" from H. L. Pattison, Esq.
" Two Specimens of Essential Oil of Bitter Almonds :" from George Whipple, Esq.
" The American Journal of Science and Arts for May, 1852 :" from the Editors.
" The Journal of the Franklin Institute for February, March, and April :" from the Institute.
" The Pharmaceutical Journal for June :" from the Editor.
" The Literary Gazette for May 22nd and 29th, and June 5th :" from the Publishers.
" A Pamphlet on Cotton, Flax, &c., and their Bleaching ; and on the Oxides and Nitrates of Lead ; and Reports on the Examination

of the Supply of Water to the Town of Preston :" from F. Crace Calvert, Esq.

A resolution of the Council was read, recommending to the Society that the names of thirteen Fellows, whose subscriptions are more than four years in arrears, be removed from the list of Fellows, in accordance with the By-laws of the Society.

The following communications were read :

1. "A note from Mr. Pepper relating to a paper read at the preceding Meeting on a New Test for Strychnine."

2. "A note on the Existence of Strontia in the Well-Waters of Bristol :" by William and Thornton J. Herapath.

3. "On the Analysis of Chrome Ores :" by F. Crace Calvert.

4. "On certain Isomeric Transformations of Fats :" by Patrick Duffy.

5. "On the Qualitative Separation of Arsenic, Tin and Antimony :" by George F. Ansell.

June 21, 1852.

Professor DAUBENY, President, in the Chair.

Alfred Smee, Esq., was admitted a Fellow.

The following donations were announced :

"Specimens of Chloride of Platosammonium, Chloride of Diplatosammonium, Chloride of Diplatosammonium and Copper, Chloride of Diplatosammonium and Lead, Bichromate of Diplatosamine, Salt of Magnus, Salt of Gros :" from G. B. Buckton, Esq.

"The Quarterly Journal of the Geological Society for May, 1852 :" from the Society.

"The Nineteenth Annual Report of the Royal Cornwall Polytechnic Society :" from the Society.

"The Literary Gazette for June 12th and 19th :" from the Publishers.

The following papers were read:

1. "Observations upon a New Series of Double Chlorides containing Diplatosammonium:" by G. B. Buckton, F.L.S.

2. "On the Action of Iodine on Phosphorus:" by B. C. Brodie, F.R.S.

3. "On the Acid Oxalates of the Earths:" by Edward Clapton.

4. "Researches on the Anhydrous Organic Acids:" by Charles Gerhardt.

NOTICES

Papers contained in other Journals.

Report upon the Alleged Adulteration of Pale Ales by Strychnine. By Professors Graham and Hofmann.

Having undertaken at the request of Mr. Allsopp an inquiry into the purity of bitter beer, with particular reference to its alleged adulteration by strychnine, we now submit the results which we have obtained upon the subject.

Strychnine or strychnia, the alleged substitute for the hop, is a fine crystallizable substance, extracted from *nux vomica*, and belonging to the class of vegetable principles termed alkaloids, of which quinine from Peruvian bark, and morphine from opium, are the most familiar examples. These substances, although susceptible of the most valuable medical application in small doses, are, generally speaking, remarkable for their energy as poisons, and for the intense bitterness of their taste; two properties which are developed in strychnine in the highest degree. Half a grain of the latter substance would poison and the bitterness of the same minute quantity is perceptible in every drop of six or eight gallons of water in which it is dissolved.

It may be stated at once, that the quantity of strychnine, which we find necessary to impart to beer the degree of bitterness possessed by pale ales, is for a gallon of beer one grain of strychnine, or double the fatal dose. The price of strychnine is about 16*s.* the ounce, which does not amount to so much as one penny per grain. Estimating the annual production of pale ale in Burton as 200,000 barrels, the strychnine required as a bitter would, however, amount to 16,448 ounces, and cost £13,158; while nobody believes that so much as 1,000 ounces of strychnine are manufactured over the whole world. The bitterness obtained by means of strychnine is equal in degree to that of the hop, but very different in kind and easily distinguished when the two bitters are compared. The bitter

of the hop is immediate in its action upon the palate, is accompanied by a fragrant aroma and soon passes off; whilst that of strychnine is not so instantaneous; but when the impression is once made it is more lasting, and becomes, from its persistence, like that of a metallic salt. The bitter of strychnine is, indeed, easily distinguishable from that of the hop, when deliberately tasted.

Still it would be highly desirable to be able to identify strychnine in beer, by the actual extraction of the substance, and the application to it of a chemical test of absolute certainty. Fortunately those poisons which have the most violent action upon the animal economy possess often also the best marked reactions, or their physiological and chemical properties are equally salient. Thus arsenic and hydrocyanic acid are the most easily detected of chemical substances; and strychnine proves to be not far behind them in this respect.

A quantity of strychnine, not exceeding $\frac{1}{1000}$ of a grain, is tested and recognised to be strychnine in the following manner. The powder is moistened with a single drop of undiluted sulphuric acid, and a small fragment of chromate of potash placed in the liquid. A beautiful and most intense violet tint immediately appears at the points of contact, and is speedily diffused over the whole liquid. Although most intense, the colour disappears entirely again in a few minutes. The admixture of the smallest quantity of organic matter, however, interferes with the success of the process. In order to apply the test, in operating upon a complex liquid like beer, the strychnine must first be extracted from the liquid and obtained in a pure or nearly pure condition. This difficulty, which appears at first considerable, may be readily surmounted, and the strychnine, if it really exist in beer, be separated, and its nature established in the most certain manner.

For this purpose, two ounces of ivory-black, or animal charcoal were shaken in half a gallon of beer to which ½ grain of strychnine had been purposely added. After standing over night, the liquid was found to be nearly deprived of all bitterness; the strychnine being absorbed by the charcoal. The liquid was now passed through a paper-filter, upon which the charcoal containing the strychnine was collected and drained.

The next step was to separate the strychnine from the charcoal. This was readily effected by boiling the mixture for half an hour in eight ounces of ordinary spirits of wine, avoiding loss of alcohol by evaporation. The spirits which now contained the strychnine were next filtered, and afterwards submitted to distillation. A watery fluid remained behind, holding the strychnine in solution, but not sufficiently pure for the test. The final purification was accomplished by adding a few drops of potash to the watery fluid, and then shaking it with an ounce of ether. A portion of the ethereal solution evaporated upon a watch-glass, left a whitish solid mass of intense bitter-

ness, and this was recognised to be strychnine, by giving the violet tint previously described, upon the application to it of sulphuric acid and chromate of potash.

Having satisfied ourselves by repeated experiments with samples of beer to which strychnine had been previously added, of the never-failing efficiency of the above method of extraction, we now proceeded to the actual examination of the commercial article. With this object, a series of samples were taken indiscriminately from the stores of a considerable number of the London bottlers, who supply the public with Allsopp's pale ale.

It may be stated, that with the exception of five varieties, the casks from which these samples were taken had all been received in London before the 20th of March, *i. e.*, the period when the possible use of strychnine in the manufacture of bitter beer was first brought before the English public.

Not one of these varieties of beer, when tested with the greatest scrupulousness, gave the slightest evidence of the presence of strychnine.

The charge of adulteration of beer by strychnine has been proposed in a manner so vague, that it is difficult to fix it, and try its validity. The existence of the adulteration is not alleged in any particular sample of beer, nor the practice ascribed to any individual brewer or dealer. An English journalist adopts the charge, upon the report that such an opinion is entertained and expressed by a French chemist of distinction, M. Payen, in his public lectures at Paris. From this gentleman we have since obtained explanations which define more closely the kind of charge which was actually made by him. The late M. Pelletier, the well-known manufacturer of organic products in France, had received at one time an order for an extraordinary quantity of strychnine, of which the destination was at first unknown to him ; but which he afterwards learned had been entirely exported to England, and used, as he informed M. Payen, to complete the bitter of certain kinds of beer.

We have reason to know, although it is not stated by M. Payen, that these remarks of Pelletier refer to a period ten or twelve years past ; and further, although not informed of the amount of the order, we have good authority to state that fifty or a hundred ounces would have been considered a large order for strychnine at that time. The calculation already given, shows how utterly insignificant such a supply of strychnine would be for its imagined application in the pale ale breweries. It is likewise known that the manufacture of strychnine has not been on the increase in France of late years.

M. Payen excuses his statements on the ground that similar suspicions are conveyed in a French work, on " Adulterations and Falsifications," by Chevallier, published nearly a year ago, but which

have not hitherto received any formal contradiction in England. Notwithstanding the latter circumstance, our distinguished correspondent concludes by expressing his regret that he ever said "that the fraud appeared to have been practised," although he had added the remark at the time, "that this falsification had no doubt ceased."

It thus appears, that the charge which has been put into the mouth of M. Payen, was never made at all by that gentleman, so far as it applies to the present practice of English brewers, and with reference to anterior times, that the charge reposes simply and exclusively upon the privately expressed opinion of a deceased chemist, the grounds of which are entirely unknown to the world, and must ever remain so.

In conclusion, it is scarcely necessary to refer to the sifting nature of the chemical examination which the beers of Messrs. Allsopp's manufacture for many months past, have been subjected to, and which establish their incontestable purity. Indeed, no one who has witnessed, as we have done, the open manner and gigantic scale in which the operations are conducted in their establishment, could entertain the idea for a moment, that any practice involving concealment was possible. But even in the absence of all such scrutiny, the idea of strychnine being mixed with beer anywhere, or in any circumstances, involves an amount of improbability which might well dispel all suspicion on the subject.

There is an act of Henry VII., which prohibits the *adulteration* of ale by brimstone or *hops*. The place of the hop was then supplied by sage, horehound, chamomile, and other indigenous bitter plants. Since that period, the character of the national beverage must have undergone a silent revolution, for all varieties of beer, both pale and brown, now owe their distinctive properties to the hops which are boiled in the malt-infusion, and fermented along with it, as completely as wine owes its peculiar character to the grape. Substitute any other bitter for the hop, and the fermented wort would no longer be recognised as beer.

Were mere bitters all that is required, it would be easy to prove that the extract of quassia would supply a bitter which is perfectly harmless and agreeable, and infinitely less expensive than strychnine.

But the process of brewing pale ale is one in which nothing but water, the best malt and hops, of the first quality are used, and is an operation of the greatest delicacy and care, which would be entirely ruined by any tampering with the materials employed. Strychnine could not fail to be rejected, from the ungrateful, metallic character of its bitterness, independent of all objections of a more serious kind. This peculiarity of taste is also calculated to betray its presence. Small, too, as the proportion of strychnine may be, which is necessary to impart the degree of bitterness of pale ale, the quantity rises, as has been seen, to a poisonous dose in half a gallon of the fluid;

and as this poison is one of those which are known to accumulate in the system, its poisonous action would inevitably follow, in occasional cases, upon the consumption of much smaller portions of beer when continued for many days without intermission. The violent tetanic symptoms of poisoning by strychnine are also such as could scarcely fail to excite suspicion and alarm. Add to these disadvantages, the certainty of the means of detecting strychnine in beer by the chemical tests described above, which any medical man or practical chemist can apply, and the chance of the use of so dangerous a substance for any purpose of adulteration, becomes in the last degree improbable.

On the Polarizing Crystals produced by the action of Iodine on the Sulphate of Quinine.*

By Dr. Herapath.

(ABSTRACTED BY THE AUTHOR.)

In March last, Dr. Herapath announced the discovery of a beautiful crystalline compound, possessing the optical properties of the tourmaline, and even in a superior degree to this mineral. It also, at certain angles of rotation, would act as selenite, viz., depolarize a ray.

This remarkable body was procured in the following way:

About 10 grains of di-sulphate of quinine were dissolved in half a fluid ounce of pure acetic acid, and gently warmed; a spirituous solution of iodine was then cautiously added, a few drops at a time; the whole again gently heated to dissolve the cinnamon-brown precipitate first produced, and the mixture set aside for several hours to crystallize.

When these crystals were examined by reflected light, they were found to possess a brilliant emerald-green colour, similar to murexide, or the fragments of the elytra of cantharides; but by transmitted light, they were almost colourless and transparent, having a slightly olive-green tint only.

The forms of these crystals are very various: prismatic plates, parallelopipeds, rhomboidal parallelograms, and hexagonal plates very perfect; but by very careful manipulation and slow crystallization, the author obtained large compound plates composed of many flat prisms, joined edge to edge, and all in the same plane; by which means he was enabled to produce crystals large enough to furnish his microscope with artificial tourmalines, and to perform all the experiments usually exhibited by the polarizing microscope.

* Phil. Mag. and Pharm. J. [4], III, 161.

Upon submitting this substance to chemical analysis, he discovered the fact of its being a compound of iodine, sulphuric acid, and quinine; many experiments prove that all these constituents are absolutely essential to its production, and the removal of either will destroy the compound.

At first Dr. Herapath proposed the name of *iodide of disulphate of quinine;* but a recent quantitative analysis has occasioned a change in the idea of its constitution, and he now proposes that of *sulphate of iodo-quinine.*

Similar experiments were made with other vegetable substances, especially alkaloids, viz., quinidine (β-quinine), cinchonine, brucine, strychnine, morphine, and salicine, but without success.

The chemical characters of this salt are the following:

The crystals are immediately dissolved, upon heating the mother-liquid to 180° F. (82⅔ C.), but recrystallize on cooling. They are dissolved by diluted sulphuric acid, upon exposure to air on a plate of glass. Distilled water also has a disintegrating action on them. Alcohol, boiling, dissolves them readily. They partially fall again, on cooling, but altered in form. They are now rosettes, composed of small hexagonal plates. Ether and chloroform have no action on them. Ammonia destroys them directly. They become opaque, and orange-yellow, the iodine and sulphuric acid being both partially removed, quinine and iodine remaining combined.

The primary form of this crystalline substance appears to be the rhombic prism.

The optical properties present many most interesting peculiarities, and to observe them, a power of 100 diameters is necessary.

1. When two crystals are crossed at right angles, the space where they are superimposed is as dark as midnight, or slightly brown, according to the thickening of the plates. (Figs. 1, 2, 3, 4 and 6.)

FIG. 1.   FIG. 2.
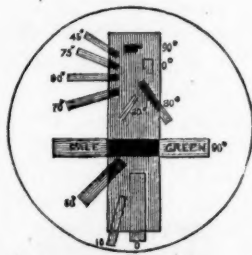
2. When two prisms are superposed, but perfectly parallel in their long diameters, the light passes through unaltered. (Figs. 2 and 3.)

3. When they cross at 45°, polarization occurs, but not so intensely as at 90°. (Figs. 2 and 4.)

4. There is a perceptible polarizing effect at 30°, but below this angle there does not appear to be any effect on transmitted light. (Fig. 2.)

5. When three crystals are examined in a superposed position : two of these being at right angles, and therefore at the maximum of polarization, the third placed between these at 45°—the phenomenon of depolarization is produced. The interposed crystal permits the light to pass through, and at the same time communicates to it the order of colour equivalent to its thickness, in the same manner as a plate of selenite would do, if introduced between two tourmalines at right angles to each other.   (Fig. 4.)
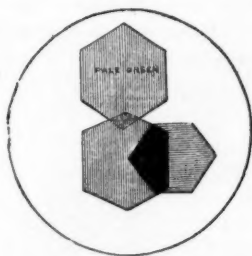
FIG. 3   FIG. 4.
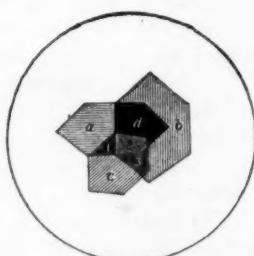
6. Upon examining two of these prisms with a single tourmaline, that one parallel to the plane of the analyser allows the light to pass through.   But the crystal which is at right angles to the plane of the tourmaline is wholly dark ; it stops the ray perfectly.   (Fig. 5.)

7. Three crystals arranged in the following way are examined by a single tourmaline above the eye-piece.   Let the inferior crystal be at right angles to the tourmaline, the two superior crystals crossing each other at 90°, but each intersecting the inferior at 45° ; polarization takes place between the inferior crystal and the tourmaline ; but the two intermediate crystals depolarize, where they intersect the inferior crystal ; polarize where they cross each other at 90°. (Fig. 6.)

FIG. 5.   FIG. 6.
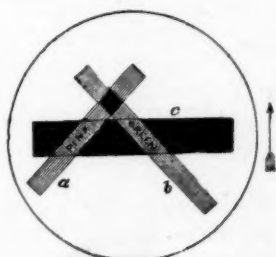
8. Upon examining two of these crystals, crossing each other at

90° in the polarizing microscope, the two tourmalines being crossed at 90°, of course the field will be dark ; and if the crystals coincide with the planes, they will not be visible, at least the only evidence of their existence in the field will be a greater intensity in the darkness ; but upon revolving the crystals through an arc of 45°, they directly depolarize the light, and of course permit it to pass through the superior tourmaline.

9. The most remarkable effect is discovered in examining this object by means of a single and inferior tourmaline, with a selenite stage placed upon it (this arrangement occupies the stage of the microscope) ; on placing the new crystals in the field, we observe that all those which are parallel to the plane of the tourmaline are brilliant green, all those at right angles are vivid red or wine-colour—supposing the stage to be the red selenite. Revolve the object through 45°, and they become both slightly olive-green.

FIG. 7.   FIG. 8.
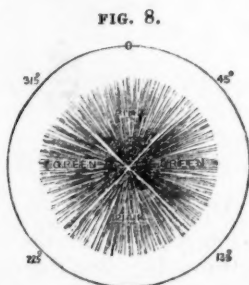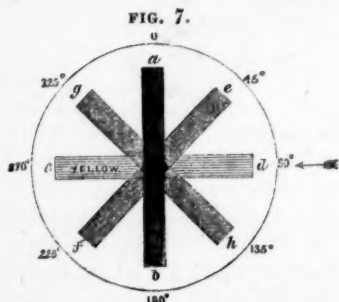
10. Upon replacing the red selenite by a film exhibiting the blue tint, then that crystal which is at right angles to the polarizing plate of tourmaline, developes the blue colour of the stage, whilst that which is parallel to the tourmaline, exhibits the complementary yellow (Fig. 7). Upon revolving the object 45°, the two crystals become nearly of a neutral-tint. If these crystals are superposed in these experiments, the space where they cross is necessarily dark.

11. The same phenomena are exhibited by the hexagon, and all other forms of the crystals.

12. The single tourmaline and the selenite stage are thus exceedingly delicate tests of the power which substances possess of *polarizing* light; the author has, by its means, discovered that many substances possess the power, as disulphate of quinidine (β-quinine) (Fig. 8); this is much more intense in its power than the disulphate of quinine, and has been used as a means of discriminating them.

13. The next experiment to which the new crystals were submitted was the usual arrangement of the polarizing microscope, viz.: *two*

tourmalines at 90°, and the selenite stage (pink)—of course the whole field of the microscope is pink or wine coloured.

Upon introducing the object, all those crystals which are at right angles to the analyzing or superior plate of tourmaline, are intensely dark brown, or black, according to their thickness. All those which are parallel to the same tourmaline allow the pink colour of the stage to pass through them; whilst those which are from 45° to 225°, and from the points 315° to 135°, are green or yellowish; they are in the plane of depolarization, and add their crystalline thickness to the selenite stage. (Fig. 9.)

FIG. 9.
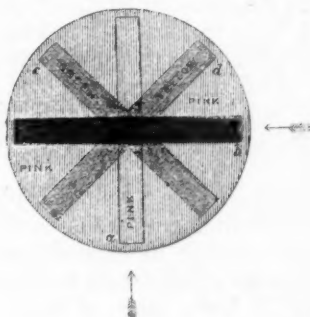
14. Upon replacing the pink stage with a blue plate, the whole field will, of course, be intensely blue; introduce the object, the crystals at right angles to the upper tourmaline will polarize, and produce a dark brown or black as before. Those parallel to it will allow the blue colour to pass through them.

The two crystals (45° to 225°) and (315 to 135°) will be violet and orange-yellow respectively, being complementary in colour to each other.

15. Upon revolving the superior tourmaline in the two last experiments, the whole appearance changes; the field becomes in one case green, and yellow in the second instance, and the crystals change colours also; but the principles involved are the same in both experiments.

16. Not only do these crystals polarize light by *transmission*, but when used as reflecting surfaces, they also alter the ray and reflect a beam polarized in one plane when the light is incident upon them at an angle of 41°.

17. It has been already stated, that the author has succeeded in adapting one of these artificial polarizing crystals to the stage of his microscope; it is sufficiently large to give an uniform tint to the whole field, and covers a surface ⅛th of an inch in diameter. This will bear magnifying to any extent; and he has been enabled to illuminate

a field of 11 inches in diameter with light polarized by its means. Since this period, Dr. Herapath has succeeded in making one large enough to surmount the eye-piece of his instrument, so that he is now perfectly independent of the tourmaline and Nichol's prism in all his experiments on polarized light; his artificial crystals possess some advantages over the natural tourmalines, in giving much more brilliant colours than when two tourmalines are employed; and as an ocular analyser, it is superior to the Nichol's prism, as it gives a larger field when properly mounted.

18. When the sulphate of quinine happens to crystallize in radiating prisms beneath the large compound plates, as it will readily do if there be an excess in the mother liquid, a splendid object is obtained, not to be equalled by any known combination. Upon placing a selenite stage beneath this object, the plate becomes coloured according to the thickness of the stage, and the angle of the crystal's rotation, whilst the sulphate of quinine exhibits all the splendour of the rainbow. The analysing plate of tourmaline is not employed above the eye-piece.

19. Upon submitting these artificial plates to micrometrical measurement, it was found that those which possessed sufficient thickness to adhere together in clusters, and to raise themselves upon their edges so as to exhibit their thickness, were none of them more than $\frac{1}{300}$th of an inch, many of them $\frac{1}{600}$th or $\frac{1}{900}$th of an inch only; but even these were much thicker than any of the broad, thin plates, so readily broken, some of which were successfully mounted; these could not have been more than $\frac{1}{1000}$th of an inch; and when it is recollected, that tourmalines, as sold for optical purposes, are generally from $\frac{1}{100}$th to $\frac{1}{50}$th of an inch, it is at once apparent that this newly-discovered salt of the vegetable alkaloid quinine, is the most powerful substance known as a polarizing crystal.

QUANTITATIVE ANALYSIS.

Having previously satisfied himself that iodine, sulphuric acid and quinine entered into the composition of the crystals, the author undertook the quantitative analysis; but before attempting this, it was of course necessary to invent a process which would furnish a large quantity of this substance at one operation. After several attempts, with more or less success, the following method was adopted, which, at the same time, served as a means of corroborating the results of the future analysis, as it enabled the experimenter to account for all the iodine used in the operation.

A tubulated retort was adapted to a receiver by careful connections, and the latter adjusted to a second receiver, somewhat in the manner of a Wolff's apparatus; the condensers were then surrounded

by a freezing mixture of nitrate of potash and chloride of ammonium.

Into the retort were placed 100 grains of pure disulphate of quinine, with three fluid ounces of acetic acid; two drachms of diluted sulphuric acid (containing about twelve grains of dry acid). When this mixture had been raised to 110° Fahr. (43⅓° C.), the alcoholic solution of iodine was gradually added through a bent glass funnel adapted to the tubule of the retort. In this manner thirty grains of iodine, dissolved in 1150 grains of alcohol were employed. The whole operation occupied about half an hour, during which period a reddish-brown coloured fluid distilled and collected in the receivers — about four fluid drachms in quantity. This of course was carefully set aside for examination. The whole was allowed to become cold, still in connection; an abundant crop of crystals formed in the retort, which, having been kept during twenty-four hours at a temperature of 40° Fahr. (4⅘° C.) to deposit, were collected on a filter, and washed several times with acetic acid at 40° Fahr., which had been previously found to have little solvent power on this compound at that temperature. The crystals having been well washed, were dissolved in boiling alcohol, sp. gr. 0·838, and, on cooling, they recrystallized; this operation being repeated, they were at length obtained pure from any admixture of disulphate of quinine. Having been drained on a filter and washed with cold spirit, they were dried at 90° Fahr., (32⅖° C.) and subsequently over sulphuric acid and weighed. By this operation 66·6 grains were obtained.

The acid mother-liquid, together with the first washings, was then examined for iodine. Upon allowing a few drops to evaporate spontaneously on a slip of glass, polarizing crystals formed around the edge of the liquid; consequently the compound is slightly soluble in cold acetic acid and spirit. The acetic acid having been nearly neutralized by ammonia, nitrate of silver was dropped into the solution as long as any iodide of silver was deposited. This was then carefully collected on a filter; washed repeatedly with distilled water; then with ammonia to remove any chloride; again with distilled water; then dried, ignited, and weighed; it gave 2·00 grains=iodine 1·08 grains.

The alcoholic mother-liquids and washings were then examined for iodine; crystals were similarly obtained upon spontaneous evaporation. In order to precipitate the iodine, a solution of silver was used, and dropped into the fluid as long as any cloudiness was produced; the whole thrown on a filter; and the precipitated iodide of silver washed with diluted nitric acid to remove any quinine, subsequently with ammonia to take up any chloride, and then again with distilled water. Dried, ignited, and weighed, it gave 3·63 grains=1·951 grains of iodine.

It now remained to examine the distilled liquids for iodine; as it

existed in these in the free state, dissolved in alcohol, they were
mixed together and a little water added, and placed in a counterpoised
flask with metallic zinc.   After prolonged digestion, the iodine was
converted into iodide of zinc; the fluids were then distilled off and
the iodide of zinc dried at 100° C. and weighed; it gave 3·35 grains =
2·6715 grains of iodine.

Now if any substitution-compound had been formed by the action
of the iodine on the quinine, it was probable that hydriodic ether
would have been produced; if so, it would be found in the distilled
fluid.   This was carefully examined for this substance, but none
detected; subsequent experiments showed that none could have been
produced, or if any, so small in quantity that its presence would be
immaterial; for all the iodine used, with the exception of 2·56 grains,
can be accounted for thus :

21·7375 grains iodine in the 66·6 grains of crystals.   (Calculated
                          at 32·63 per cent., as found subsequently.)
1·0800   „   iodine in the acetic mother-liquid (crystals).
1·9510   „   iodine in the alcoholic mother-liquid (ditto).
2·6715   „   iodine in the distilled fluid as free.

27·4400

2·56   grains iodine lost.   This was lost in drying the crystals
by expression between folds of bibulous paper.

Had a substitution-compound been formed, one-half of the iodine
should have formed hydriodic acid; the other half should have been
in the crystalline compound, as the substitution-base; therefore, it is
evident that no such substitution-base can be the result.

One other question arises—Does the iodine exist in the green
crystals as hydriodic acid ?

Some of the crystals were dissolved in *diluted* alcohol (boiling)
and starch added to the liquid still warm; instantly an abundant
precipitation of the blue iodide of amidine occurred; starch was
added in excess, and until no further indications of iodine were
evident; the colourless fluid was then separated by decantation, and
tested with nitrate of silver : not the least trace of hydriodic acid, or
any soluble iodide was apparent.   Similar results were obtained when
the crystals were dissolved in hot acetic acid and tested with starch.
It is evident, therefore, that no hydriodic acid is present in the
crystals; and consequently, that the iodine cannot exist in the com-
pound as a substitution-base, or even as hydriodic acid.

The iodine separating so readily in the free state, upon dissolving
the crystals in alcohol, or in acetic acid, rendered it a somewhat
difficult matter to estimate it correctly : starch was first used as the
precipitant : the resulting iodide of amidine decomposed by sul-
phuretted hydrogen, the hydriodic acid produced, neutralized by

ammonia, this precipitated by nitrate of silver, and the resultant iodide of silver estimated; but accuracy was far from being obtained by this method, in consequence of iodine subliming during the solution of the crystals.

(*a*) At length it was found that by passing a current of washed and pure sulphuretted hydrogen through acetic acid, in which a known quantity of crystals had been placed, and applying heat to the mixture as soon as the gas began to be evolved, the iodine was converted into hydriodic acid as soon as it was liberated from the crystals. The decomposition being perfect, and the operation finished, the excess of sulphuretted hydrogen was expelled by boiling, testing with acetate-of-lead-paper from time to time during this part of the process; the precipitated sulphur removed by filtering, and well washed with distilled water; ammonia added to the filtrate nearly to neutralization, but short of precipitating the quinine; the solution boiled, and the iodine precipitated by nitrate of silver; the precipitate collected on a filter, washed with distilled water, then with diluted nitric acid (to remove any quinine which falls with iodide of silver even from an acid solution), and lastly, dried and fused by ignition in a platinum capsule. Twenty-five grains of crystals gave by this method 15·14 grains of iodide of silver $= 8·1523$ grains of iodine $= 32·6092$ per cent.

(β) The solution, after the separation of iodine, was then, together with the washings, treated with acetate of baryta, until no further deposition of sulphate occurred; it was boiled to hasten the separation, filtered, washed, dried, and ignited; it weighed 7·76 grains $= 2·653$ $SO_3 = 10·612$ per cent of sulphuric acid.

(γ) The liquid, after the separation of iodine and the sulphuric acid, was then acted on, first by sulphate of ammonia to remove excess of baryta, then with hydrochlorate of ammonia to remove the excess of silver.

(δ). To this fluid, concentrated by evaporation to about three fluid ounces, ammonia was added in excess; an immediate deposition of the alkaloid was the consequence. Ether was now added in sufficient quantity to dissolve the alkaloid; the supernatant ethereal fluid was decanted into a counterpoised flask, the operation being repeated as often as necessary; the mixed ethereal fluids distilled; and the residuary alkaloid dried at 100° C.: it gave 7·533 grains.

(ϵ). The aqueous and ammoniacal solution, upon evaporation to dryness in a water-bath, and again treating the residue with ether as long as necessary, and distilling as before, furnished a second quantity of the alkaloid, which, dried at 100° C. as before, weighed 3·14 grains.

Then $7·533 + 3·14 = 10·673$ alkaloid equal to 42·692 per cent.

This analysis, therefore, accounts for—

$$\begin{array}{lr}
\text{Iodine} & 32 \cdot 6092 \\
\text{Sulphuric acid} & 10 \cdot 6120 \\
\text{Alkaloid} & 42 \cdot 6920 \\
\hline
& 85 \cdot 9132
\end{array}$$

The loss . . . . 14·0868, was possibly water of crystallization; but it now became necessary to perform an analysis to make this point certain. After several attempts, the following process was adopted, and furnished correct results.

Having arranged an apparatus for preparing a current of dry hydrogen gas, the stream was passed through a flask containing iron filings. These were then heated red-hot; the oxide of iron was reduced to the metallic state. When the gas issuing from the exit-tube of the apparatus burnt with a steady yellow flame, the operation was discontinued—at least the spirit-lamp was removed—and the iron allowed to cool, still in an atmosphere of dry hydrogen gas, and when cold, removed and well secured in a small stoppered bottle.

To the same apparatus for generating the dry hydrogen, was adapted a counterpoised test-tube (a), and to the exit-pipe from this was connected a tube (b) containing chloride of calcium, this tube with its contents being also accurately counterpoised.

Into the tube (a) was placed a mixture of 10·2 grs. of the crystals (previously dried at 100° C.) rubbed up in a mortar with 50 grains of the purified iron-filings; the mortar was wiped out carefully with twenty grains of the same iron, and this also inserted into the tube carefully; a layer of pure iron-filings was placed over the whole, and the tube with its contents and fittings accurately counterpoised.

This part of the apparatus was then placed in a flask containing a solution of chloride of zinc, destined to act as a bath. The whole apparatus having been satisfactorily adjusted, heat was now applied to the bath, and gradually raised until the chloride of zinc ceased to give off any water, and of course fused. This must have been about 420° Fah. (215° C.), or more.

In this operation, the crystals were decomposed; the iron seized the iodine as fast as it was liberated; the quinine retained the sulphuric acid; and the current of dry hydrogen gas carried off the aqueous vapour to the chloride of calcium tube, where it was retained. The increase in weight was 1·44 grains; thus, as 10·2 : 1·44 = 100 : 14·1764 grains of water per cent.

This method was also adopted as a means of estimating the iodine; but for this purpose, the chloride of zinc bath was not employed, as a more perfect decomposition was then necessary. The mass in the test-tube (a) was lixiviated repeatedly, as long as any iodide of iron dissolved; this was at once filtered into a solution of nitrate of

silver, iron filings being kept in the filter to avoid decomposition. The filter was repeatedly washed with boiling distilled water, and of course the washings were added to the previous liquid. The resulting mixture of iodide of silver and the oxides of iron was thrown on a filter, and washed with hot diluted hydrochloric acid as long as any iron was removed; then with ammonia to remove any chloride; and afterwards again with distilled water; and lastly dried, ignited, and weighed: it gave 6·00 grains = iodine 3·1453 and 31·453 gr. per cent, a result corresponding very closely with that previously obtained.

A second analysis specially directed to the estimation of the sulphuric acid, gave 10·844 per cent as the result. Therefore we now have :

	(α)	(β)		Calculated.
Iodine. . . .	32·6092	31·453	124	32·6300 . . 1 at.
Sulphuric acid .	10·6120	10·844	40	10·5200 . . 1 at.
Alkaloid . . .	42·6920	—	162	42.6300 . . 1 at.
Water	14·1764	—	54	14·2152 . . 6 at.
	100·0896		380	99·9952

These results correspond closely with the formula

$$(C_{20} H_{12} NO_2 + I) + SO_3 + 6 HO ;$$
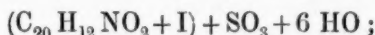
and as it has been previously proved that the base is not a substitution-compound, it only remains to consider it a salt in which iodine is super-added to the base quinine without interfering with its basic properties, however much it might alter its chemical characters.

Experiments have been instituted to produce this iodo-quinine in an isolated state, but hitherto without success; the nearest approach hitherto made, is by the action of ammonia at 60° Fah. (15⅓° C.), by carefully triturating the polarizing crystals in the strongest liquor ammoniæ during half an hour; separating on a filter; washing with cold distilled water; and carefully drying the reddish-yellow mass produced. This contained *nearly* all the iodine and quinine; but the ammoniacal solution contained sulphate of ammonia, with some of the resinous compound dissolved in it, together with about 11·0 per cent of hydriodate of ammonia. The action of iodine on the acetate of quinine has also been tried, and the iodo-quinine has been produced; but it does not act as a base should do, namely, dissolve in acids at once without decomposition.

The resinous mass was treated with diluted sulphuric acid, in order to reproduce the polarizing crystals; they certainly were formed, but not in a satisfactory manner; some other compounds were also produced, the formation of which cannot be accounted for in the present state of the question. The alkaloid separated by the pre-

viously detailed analysis was examined; from it was first made the disulphate; this differed materially from disulphate of quinine, both in its crystalline form and its solubility.   It would dissolve in about three times its weight of water, at 100° C., crystallizing in radiating plumose tufts, very similar to acetate of morphine in appearance. From this disulphate were reproduced the polarizing crystals very readily upon submitting it to the same operation as was originally used, namely, solution in acetic acid, and adding a spirituous solution of iodine to the heated fluid; on cooling, the green crystals were deposited, having their original extraordinary properties.   The disulphate of the alkaloid differed as much in its optical as in its chemical characters from quinine; assimilating itself in the former to the disulphate of quinidine (β-quinine); whereas the pure alkaloid much more resembled quinine in its chemical characters, as it is soluble both in alcohol and ether, but crystallizes from neither with facility.   Some slight appearance of crystallization is obtained by exposing an alcoholic solution to spontaneous evaporation in a test-tube; around the edge of the liquid, a thin radiating plumose crop is produced, more distinctly acicular than the disulphate.   It is, therefore, not quinidine (β-quinine), but is probably similar to that variety of quinine recently called γ-quinine by J. Van Heijningen,* a monohydrate of the organic compound $C_{20} H_{12} N O_2$, of which a-quinine is the tri-hydrate, and β-quinine or quinidine the bi-hydrate.

However, further researches are necessary to establish this point; for the present we are justified, from the reproduction of the polarizing crystals from the alkaloid separated from the green polarizing compound by analysis, in considering that the alkaloid quinine enters into the composition of the crystals,—in the character of an iodo-base,—*not* a substitution-base, as has been already shown, but a compound analogous in its constitution to iodo-codeine, dicyano-codeine, cyaniline, cyano-toluidine, and cyano-cumidine, all of which are compounds not belonging to the series of substitution-products. This, if correct, is a remarkable circumstance, and worthy of verification by a more elaborate investigation.

* Pharm. J. January, 1850.

On a Method of obtaining a perfect Vacuum in the Receiver of an Air-pump.

By Thomas Andrews, M.D., F.R.S., M.R.I.A.*

The space left vacant in the upper part of a long glass tube, which, after being filled with mercury, is inverted in a basin of the same metal, affords the nearest approach to a perfect vacuum which has hitherto been obtained. It is true that it contains a little mercurial vapour at the ordinary temperature of our summers, and probably also at lower temperatures; but the quantity is exceedingly small, and its influence in depressing the barometric column must be altogether inappreciable. Besides the mercurial vapour, a trace of air may generally be detected, even in tubes which have been carefully filled, and in which the air interposed between the glass and mercury has been expelled by ebullition. This is best observed by inclining the tube till the mercury comes into contact with the upper end, when any air that may have been diffused through the vacuum will be seen collected in a small bubble, but greatly rarefied. It is easy to calculate approximately the depression of the mercurial column produced by this residual air. For this purpose, the tube must be inclined till the bubble is exposed to a pressure of a few inches of mercury, measured in a vertical direction. In this position its apparent diameter is measured, as also the pressure to which it is exposed. For the object in view, the volume of the bubble may be calculated on the assumption that it is a sphere. The space occupied by the vacuum must also be estimated; and with these data, the depression of the mercurial column may easily be calculated.

Let V be the volume of the space above the mercury when the tube is vertical;

p, the pressure under which the diameter of the bubble of air has been measured;

r, the semidiameter of the bubble;

x, the depression of the mercurial column.

Then

$$x = \frac{4}{3} r^3 . \pi p \, \frac{1}{V}.$$

If the diameter of the bubble, $2r$, be 0·02 inch, the pressure p, 2 inches, and the space V, 1·2 cubic inch, the value of x is nearly

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* Phil. Mag. [4], III, 104.

0·00001 inch ; or the depression of the mercury, in consequence of
the vacuum not being absolutely perfect, amounts only to $\frac{1}{100,000}$ of
an inch.   It is easy in actual practice to realize this close approxima-
tion to a perfect vacuum.   The quantities now stated apply, in fact,
to a barometric tube employed in an experiment which will be subse-
quently described.

The Torricellian vacuum leaves therefore scarcely anything to be
desired in point of completeness; but it is unfortunately applicable to
very few physical investigations.   No instrument of any kind can be
introduced into it, nor even any substance which is acted on by
mercury.   The vacuum obtained by the exhausting pump is not liable
to these objections; but even with machines of the most perfect con-
struction, and in the best order, only a very imperfect approach can be
attained to a complete exhaustion.   A good ordinary pump with silk
valves seldom produces an exhaustion of 0·2 inch ; and it is very rare
indeed, if the manometer is properly constructed, to have it carried to
0·1 inch.   In his " Etudes Hygrométriques,"* M. Regnault has
given the following method for pushing the exhaustion further after
the valves have ceased to act.   In a large glass globe of from 20 to
25 litres capacity (4½ to 5½ English gallons), he places an hermetically
sealed capsule of glass containing from 40 to 50 grms. of sulphuric
acid.   He also introduces into the globe 2 or 3 grms. of water, and
exhausts till the water has entirely disappeared and the machine
ceases to act.   By agitating the globe, the capsule is ruptured; and
the sulphuric acid coming into contact with the vapour of water,
which has displaced nearly all the residual air in the receiver,
condenses it and leaves a vacuum nearly perfect.   This globe thus
exhausted is next placed in communication with the apparatus in
which a very perfect vacuum is desired, taking care to remove the air
from the interior of the connecting tubes.   On opening the stop-
cocks, the air becomes uniformly diffused through the two spaces ; and
if the capacity of the globe is considerable, compared with that of the
other vessel, the elastic force of the air may be reduced to a small
fraction of a millimetre.   If, on the contrary, the capacity of the latter
is considerable, this operation must be repeated several times.

This ingenious process is not adapted to give a very perfect vacuum
in the second vessel, unless the operation be repeated several times,
which would be exceedingly laborious.   It is also liable to other
difficulties in the execution, which will at once occur to any one
accustomed to experiments of this kind.   Besides, it does not afford
the means of obtaining a vacuum, which, as far as the indications of a
mercurial manometer can be observed, is perfect; as in M. Reg-
nault's observations, the elastic force of the air was still capable of

* Ann. Ch. Phys. [3], XV, 190.

measurement, although only amounting to a small fraction of a millimetre.

By using the necessary precautions, a vacuum may be obtained by the following process, with very little trouble, in the ordinary receiver of an air-pump, so perfect that the residual air exerts no appreciable elastic force.   Even after this limit has been reached, the exhaustion may be pushed still further, till it must become at last not less complete than the Torricellian vacuum; while at the same time, by suppressing the manometer, the existence of mercurial vapour may be altogether prevented.   The manipulations required to arrive at this result will not interfere with the presence of the most delicate instruments in the receiver.

Into the receiver of an ordinary air-pump, which is not required to exhaust further than to 0·3 inch, or even 0·5 inch, but which must retain the exhaustion perfectly for any length of time, two open vessels are introduced, one of which may be conveniently placed above the other; the lower vessel containing concentrated sulphuric acid, the upper a thin layer of a solution of caustic potash, which has been recently concentrated by ebullition.   The precise quantities of these liquids is not a matter of importance, provided they are so adjusted that the acid is capable of desiccating completely the potash solution without becoming itself notably diminished in strength, but at the same time does not expose so large a surface, as to convert the potash into a dry mass in less than five or six hours at the least.   The pump is in the first place worked, till the air in the receiver has an elastic force of 0·3 or 0·4 inch, and the stop-cock below the plate is then closed.   A communication is now established between the tube for admitting air below the valves and a gas-holder containing carbonic acid, which has been carefully prepared so as to exclude the presence of atmospheric air.   After all the air has been completely removed from the connecting tubes by alternately exhausting and admitting carbonic acid, the stop-cock below the plate is opened and the carbonic acid allowed to pass into the receiver.   The exhaustion is again quickly performed to about the extent of half an inch or less. If a very perfect vacuum is desired, this operation may be again repeated; and if extreme accuracy is required, it may be performed a third time.   It is not likely that anything would be gained by carrying the process further.   On leaving the apparatus to itself, the carbonic acid which has displaced the residual air is absorbed by the alkaline solution, and the aqueous vapour is afterwards removed by the sulphuric acid.   The vacuum thus obtained is so perfect, that even after two operations it exercises no appreciable tension.

To give a clear conception of the progress of the absorption, I will describe in detail one observation in which the tension was measured simultaneously by a good syphon-gauge and by a manometer, formed

of a barometric tube 0·5 inch in diameter, inverted in the same reservoir of mercury as a similar tube communicating with the interior of the receiver.   The barometer had been carefully filled, and the depression of the mercury estimated by the method already described at less than $\frac{1}{100,000}$ of an inch.

Previous to the admission of the carbonic acid, the exhaustion was carried only to 0·4 inch; it was again carried to 1 inch; and a third time to 0·5 inch, after which the apparatus was left to itself.   The manometer indicated a pressure in—

> 15′ of 0·25 inch.
> 30′ „ 0·17 „
> 80′ „ 0·10 „
> 200′ „ 0·02 „

In twelve hours the difference of level was just perceptible, when a perfectly level surface was brought down behind the tubes till the light was just excluded.   In thirty-six hours not the slightest difference of level could be detected.   The vacuum has remained without the slightest change for fourteen days.

It is evident that the only limit to the completeness of the vacuum obtained by this process, arises from the difficulty of preparing carbonic acid gas perfectly free from air.   This may be very nearly overcome by adopting precautions which are well known to practical chemists.   When an extreme exhaustion is required, the gas-holder should be filled with recently boiled water, and the first portions of carbonic acid that are collected in it should be allowed to escape.

The substitution of phosphoric for sulphuric acid would remove the possibility of either aqueous or acid vapours being present even in the smallest amount, but such a refinement will rarely be found necessary.

In the experiment just described, the theoretical residue of air would be $\frac{1}{135,000}$ part of the entire quantity in the receiver, which would cause a depression of $\frac{1}{4,500}$ of an inch.   This result must have been nearly realized.   If the exhaustion had been carried at each time to 0·2 inch, the residue by theory would have been only $\frac{1}{3,375,000}$ part.   But the experimental results will not continue to keep pace with such small magnitudes.

XVI.—*Note on the existence of Strontia in the Well-Waters of Bristol.*

By Messrs. William Herapath and Thornton J. Herapath.

Our attention was first directed to this subject, in consequence of the discovery of a small quantity of sulphate of strontia in the deposit or crust which had formed in the interior of a pipe in connection with the hot baths at our Royal Infirmary. We subsequently found, that this compound was also contained in very minute proportion in the water with which this institution was supplied. Having been much occupied lately in examining the well-waters from different parts of the city and its suburbs, we have succeeded in assuring ourselves that the above is not an isolated case, and that sulphate of strontia occurs to a greater or smaller extent in the waters from most parts of the city, particularly in those from the neighbourhood of Cotham, Kingsdown and West Clifton, as well as on the opposite side of the city, at Pyle Hill. The liasic and marly strata which occur here, as is well known, contain fine beds of crystallized celestine, for which this district has been long celebrated. Hence, the presence of this mineral ingredient in the water is easily accounted for.

Those waters we have found to contain the largest proportion of strontia are obtained from Cotham, on the edge of the lias, and at its junction with the new red sandstone. In one specimen which we examined from this locality, we detected as much as three-tenths of a grain of the sulphate per gallon. The process of analysis pursued

in this inquiry was as follows:—The water having been evaporated to dryness, the residuary mass was heated with an excess of pure sulphuric acid, in order to convert the whole of the earthy and alkaline salts present into sulphates, and also to get rid of the organic matter. The excess of sulphuric acid was then expelled by a further application of heat, and the fixed residue extracted, first with boiling water, and subsequently with hot hydrochloric acid, until the whole of the matters that were soluble in those menstrua were dissolved out. That which remained consisted of a mixture of silica with sulphate of strontia. In order to separate these two substances, they were placed in a platinum capsule, and exposed to the vapours of hydrofluoric acid, by which means the silica was abstracted, and sulphate of strontia left behind in the pure state. The necessity for the first operation originated from the fact that the sulphate of strontia is somewhat soluble in chloride of sodium, and therefore upon attempting to estimate it, without taking the precaution to first convert the whole of the bases into sulphates, a loss would be sustained, in consequence of the solution of a part of the sulphate of strontia in the water.

We have also discovered extremely minute traces of sulphate of strontia or sulphate of baryta in many well-waters from other localities. At all events, the siliceous residue obtained by the above process, when fused with a mixture of starch and carbonate of soda, yielded a fused mass which, upon solution in water, and testing with the nitroprusside of potassium, produced a faint violet colouration, which could only be caused by the presence of a trace of alkaline sulphide, resulting from the decomposition of an earthy sulphate insoluble in hydrochloric acid.

XVII.—*A new method for the analysis of Chrome Ores.*

BY F. C. CALVERT.

It is well known to all chemists who have analysed chrome ores, what difficulties they present, and what long and tedious manipulations are required to produce satisfactory results. In the numerous analyses of chrome ores which I have made, I have found it impossible to make two analyses of the same ore satisfactorily correspond. I have, therefore, been led to make a series of experiments, the results of which I have now the honour of laying before the Society. By the results I have obtained, I believe I have removed

the objections inherent in the present mode of attacking the ore, the first of which consists in the difficulty of obtaining crucibles capable of resisting for several hours, at a high temperature, the combined actions of nitrate and carbonate of potash, but more especially of caustic potash, which it is essential to the operator to employ in order to properly attack his ore. Silver crucibles cannot stand the temperature, and those of porcelain or platinum are either dissolved or injured.

The second and most serious objection to be raised is, that owing to the high specific gravity of the ore, it falls to the bottom of the fused mass, and thus becomes excluded from the necessary oxidizing action of the atmosphere to transform the oxide of chromium into chromic acid. As the chromic acid is thus produced but very slowly, the consequence is, the ore is very imperfectly attacked, although the calcination be continued for several hours.

The first method I have employed with success, consists in mixing intimately a given quantity of the well-pulverized ore with about three or four times its weight of a mixture made by slaking quicklime with caustic soda, and then drying and calcining the mass. To the intimate mixture of soda, lime, and ore, one-fourth part of nitrate of soda is added. The whole is then well calcined for two hours, taking great care to stir the pasty mass every quarter of an hour with a platinum wire. In consequence of this mixture not becoming fluid, the ore is constantly kept in contact with the oxygen of the atmosphere, and thus becomes decomposed and the oxide of chromium oxidized. I find that, by this method, one treatment is generally sufficient to completely attack the ore. It is seldom that two treatments are necessary, whilst, by the method usually adopted, five or six successive calcinations are required. Henry Rose states that these calcinations may be avoided by weighing the remaining residuum or ore not attacked, and then calculating the chrome in it from that which has been acted upon; but this mode would lead to incorrect results, for chrome ore always contains silica and alumina, which are easily dissolved in the first operation.

The greater part of the mass is now dissolved in water, and to the insoluble portion, sulphuric acid, diluted with twice its bulk of water, is added. When the whole is removed from the crucible, a little alcohol is added to the solution, which renders the sulphate of lime nearly insoluble. The whole is next thrown on a filter and washed three or four times with weak alcohol, which dissolves all the bichromate formed, leaving the sulphate of lime with the ore not attacked on the filter. The former is easily removed by washing the filter with

boiling water. If any ore is left as a residuum, it is recalcined. The solution containing the bichromate of soda is now neutralized with ammonia and oxalate of ammonia added, which gives rise to a small precipitate of sesquioxide of iron, alumina, and oxalate of lime, together with a little silica dissolved by the excess of sulphuric acid. The precipitate having been separated, and well washed, the liquor is either boiled with alcohol to reduce the chromic acid to the state of oxide, to be precipitated and valued; or the liquor is rendered acid, and the amount of chromic acid ascertained by protochloride of tin according to Dr. Penny's process.

The two following analyses of an ore from Turkey were made by this method :

	I.	II.
Sesquioxide of chromium	57·60	58·40
Protoxide of iron	25·78	26·14
Sand, clay, chalk	17·50	16·35

Another process which I have found to produce also good results, consists in calcining the well-pulverized chrome-ore with nitrate of baryta, the oxygen of which, as it leaves it, gradually oxidizes the oxide of chromium. From time to time, towards the end of the operation, a little caustic potash is added, which facilitates the action and gives rise to chromate of potash. The transformation of the oxide of chromium into chromic acid is nicely effected by the pasty state of the fused oxide of barium preventing the ore falling to the bottom of the crucible, and thus becoming excluded from the oxidizing action of the atmosphere. On cooling, the crucible and its contents are put in contact with dilute nitric acid, which dissolves the greater portion of the mass, leaving the non-attacked ore. This residuum after being washed, is ready for a new treatment, if deemed necessary, The liquor containing the bichromates of soda and baryta, nitrate of baryta, peroxide of iron, alumina and lime, is first heated with sulphate of potash, which precipitates the baryta in the state of a sulphate. The precipitate is thrown on a filter and washed; and to the filtrate ammonia and oxalate of ammonia are added, on which peroxide of iron, alumina, and oxalate of lime fall down. The mixed precipitate is gathered on a filter, washed, and the chromium in the chromate determined.

XVIII.—*On certain Isomeric Transformations of Fats.*

By Patrick Duffy,

OF THE BIRKBECK LABORATORY, UNIVERSITY COLLEGE, LONDON.

Chevreul gave the name of stearic acid to a particular acid derivable from certain natural fats, while, at the same time, he used the word stearine as a synonyme for the most solid portion of any natural fat which furnished glycerine; thus, he speaks of the stearine of human fat, while, at the same time, he shows that stearic acid is not derivable from it. Lecanu afterwards prepared from mutton fat a substance which, on decomposition by alkalies, yielded an acid consisting chiefly of stearic acid, and proposed to restrict to this substance the name of stearine. Most chemists, adopting the principle of nomenclature contained in Lecanu's proposal, now understand the names stearine, margarine, &c., to signify bodies which, if they were obtained, would, on decomposition by alkali, furnish respectively only stearic acid, margaric acid, &c., and glycerine, and, in the absence of such substances, apply them to those which most nearly approach them. The origin of this nomenclature for the fats, belongs, however, not to Lecanu but to Chevreul; for, throughout his work on the fats, stearine is the only exception to it. This exception, I wish to remark, has been rather unfortunate: for many physiologists and some chemists, still employing the word in the sense in which Chevreul used it, have particularized by it bodies which other chemists have described as margarine or palmitine. This diversity of nomenclature has already introduced many apparent discrepancies into works upon the fats, and, as a consequence, some real difficulties in the way of further investigation. I refer to the circumstance here, not because I have any change of name to propose, but because I think allusion to it will be sufficient to render obvious the advantages of allowing stearine to signify the substance, whether hypothetical or not, which, on decomposition by alkali, affords stearic acid and glycerine, instead of forming an exception to a convenient and established system of nomenclature.

Chevreul* prepared what he called stearine from five different sources, viz., human fat, fat of swine, fat of the goose, mutton fat, and beef fat. As he gives, instead of the melting point, the point of solidification after melting, and as other chemists, in speaking of the stearine prepared by them, have given only the melting point, we are

* Recherches Chimiques sur les corps gras. Paris, 1823, p. 261, &c.

restricted to use, as the standard of comparison for their results, the melting point of the acid furnished on saponification.   The acid from the substances prepared by Chevreul, even after the removal of a portion of oleic acid, melted only in one case so high as 64·8° C. Since the melting point of stearic acid, as found by him and confirmed by others, (Redtenbacher,* Laurent and Gerhardt†) is 70°, none of the substances which he called stearine, can be regarded as a close approximation to pure stearine.

Braconnot,‡ by using essence of turpentine as the purifying agent, instead of alcohol, which Chevreul used, succeeded in procuring a substance which melted at 61·25°, and furnished an acid fusible at 62·50°.

Afterwards Lecanu§ prepared from mutton-fat, by means of ether, a substance which melted at 62°, and furnished an acid melting at 64°.   He states that he found it impossible to raise the melting point of this acid by purification higher than 66°, and adds that M. Bussy, in researches which he was then pursuing, had not found stearic acid to melt higher than 66°.   Hence he concluded that what he called stearine was a pure substance.

Since then stearine has been prepared in the same manner by Liebig and Pelouze,‖ who do not mention its melting point in their paper; by Artzbächer,¶ who brought its melting point to 60·6°, and by Heintz,** who agrees with Lecanu in its melting point. Although these chemists may not concur with Lecanu in regarding any of these substances as pure stearine, they yet admit that it is impossible to raise its melting point above 62·25°.

There are three ways in which the chemical purity of the glycerine-fats may be estimated—1st. That further crystallisation produces no change in the melting point of the fat itself; 2nd. That when crystallised, the crystallised portion and that remaining in the mother-liquor differ not at all, or only slightly, in melting point; 3rd. That on saponification, the resulting acid be not susceptible of having its melting point changed, or in other words, of further purification.

The first of these tests is that by which chemists have hitherto been guided in the purification of fats; but although competent, it

* Ann. Ch. Pharm. XXXV, 46.
† Compt. Rend. trav. chim. 1849, p. 337.
‡ Ann. Chim. XCIII, 252.   J. Pharm. XXV, [2], 307.
§ J. Pharm. XX, 325.   Ann. Ch. Phys. LV, 192.
‖ Ann. Ch. Pharm. XIX, 264.   J. pr. Chem. 173.
¶ Ann. Ch. Pharm. LXX, 239.   Compt. Rend. trav. chim. 1849, p. 343.
** Pogg. Ann. LXXXIV, 229.

is calculated to deceive unless very delicately applied, and, as will be seen, has really done so.

In the treatment of mutton fat by ether for the preparation of stearine, I have found that, although between two successive crystallisations after the fifth, the thermometer can scarcely distinguish, yet if these two crystallisations be melted under the same circumstances, a difference of time in the commencement of melting will be perceived, a difference which is still greater, the more widely separated in respect to the number of times two specimens may have been crystallised; and although the thermometer may fail to point out a difference in the melting point of two immediately successive crystallisations, yet that long after the melting point of stearine has reached 62°, the difference of melting point between substances, one of which has been crystallised two or three times oftener than the other, is quite sensible to the thermometer.

Instead, however, of relying entirely on this test, I took as guide the second, one which consists, theoretically speaking, in carrying on the crystallisation from ether, till the portion which remains in the mother-liquor, has the same melting point as that crystallised out. I say theoretically speaking: for, even after thirty-two crystallisations, the residue in the mother-liquor, after removal of a second crop of crystals, differed in melting point from the first crop by 2° or 3°.

It might be supposed that, instead of the impurities being so persistent as this represents them, the difference of melting point arose from some decomposition taking place every time the substance was dissolved; but this was not the case, for I found the melting point and composition of stearine to remain unchanged after ten weeks' contact and partial solution in ether.

Each of the thirty-two crystallisations spoken of, was made on an average with a quantity of ether at least fifty times that of the substance dissolved, and the mother-liquor was poured off when the temperature fell to 16°. At first the crystals were then washed with warm ether and afterwards strongly pressed by the hands in folds of linen; but as the substance approached to purity this was discontinued, and the mother-liquor removed by decantation alone. A second, and sometimes a third, crop of crystals was obtained from the mother-liquor, and, after being sufficiently purified, added to the first crop. In the first five or six crystallisations, the quantity of ether employed was not more than from ten to fifteen times the volume of the substance dissolved, but towards the end it was increased to upwards of one hundred times the volume. In this manner not more

than eight grammes were obtained from two kilogrammes of the crude fat.

After thirty-two crystallisations, the substance which I obtained melted, not at 62°, but at least 2° higher, and furnished an acid melting at 66°·5. It possessed characters hitherto unsuspected in the class of substances to which stearine belongs.

The method of taking the melting point consisted in fusing on a hook at the end of a platinum wire a bead of the substance, and suspending the wire in a beaker containing water previously boiled, to expel air. The temperature of the water in the beaker was regulated by placing the latter on a small sand-bath over a gas-lamp. The perfect contact between the bead and the water ensured the identity of their temperature, which was given by a thermometer suspended in the water. The temperature at which a small ring of limpid fat surrounding the bead first appeared was taken as the melting point. The melting point of substances which, like stearic acid, solidify after fusion, not in an amorphous, but in a crystalline condition, is best observed by enclosing them in thin-walled capillary tubes; for when directly exposed to the contact of the water, the latter entering the interstices among the crystals, and afterwards remaining suspended in the fused mass, gives it an opalescent appearance, and renders it difficult to distinguish the true melting point.

During the preparation of stearine in the foregoing manner, I had occasion to take its melting point at various stages of the purification. Observing that after being melted it did not, in harmony with the laws of latent heat, always solidify at the same temperature as that at which it melted, I made a register of its solidifying point in a number of cases, and found that the solidifying point was, in most cases, from 12·2° to 12·8°, and never more below the melting point, but in a few cases not even 2° below it. These observations were made long before I had brought the stearine to a state of purity; but although made on an impure substance, they remained good for the purer substance. It was next observed that these variations of the solidifying point were not due to agitation in one case, and its absence in another; in short, that in those cases in which the temperature fell 12·2° below the melting point before solidification commenced, the passage into the solid condition was not precarious; it was impossible to produce it by any mechanical means at a higher temperature. For those specimens then under examination, the conditions of these variations were found to be, that, when the temperature was raised only 1° or 2° above the melting point, solidification set in as soon as the temperature fell 1° or 2° below the melting point; but that when

the temperature was raised 4° above the melting point, solidification could be induced only when the temperature fell 12·2° below the melting point.

When the stearine which had solidified 12·2° below its melting point was again heated about 1° above the solidifying point, it became less opaque, indeed almost transparent, suggesting the impression that it was melting, but, whether the temperature remained stationary or rose, quickly resumed its opacity. Inasmuch as the precaution of enclosing the fat in dry close tubes made no difference in this phenomenon, it was concluded to be the effect of temperature alone.

In the circumstances of the foregoing experiment, where the fat was continuously heated from below to above the point at which the change presented itself, the conditions were in favour of its appearing at the lowest temperature capable of producing it. As it was shewn to be the effect of temperature, it appeared probable that if the fat were suddenly submitted to a temperature a few degrees higher, but not necessarily so high as the melting point, this appearance would present itself with greater intensity. A bead of substance, of melting point 63°, which was the purest I had at the time, was placed in a small glass tube, at one side of the part which had been previously drawn out to a capillary diameter; the tube was plunged, the end containing the bead undermost, into water at 53·6°; the air was now sucked out of the other end, whereupon the fat passed through the capillary part of the tube, which, had it not been fluid, it was impossible it could do. Hence, there remained no doubt whatever that the fat really melted at the temperature at which the forementioned transparency appeared, and afterwards solidified at the same or even at a higher temperature.*

The question now arose: is the stearine the same in every respect after as before this melting? that is, has it the same properties, and, among the rest, that of melting at this lower temperature? When taken after melting and again solidifying at 53·6°, and plunged into water at that temperature, it did not melt; in short, it melted only when the temperature rose to its ordinary melting point, 63°. The

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* Since I finished my experiments on this point, my attention has been called to the fact that Dr. Heintz, of Halle (Ber. d. Berl. A. 1849, 222.   J. pr. Chem. XLVIII, 382. L'Instit. 1849, 390) had also noticed that stearine from mutton fat, melting at 62°— 62·25°, became transparent when immersed in water at 51°—52°, and afterwards resumed its opacity when the temperature rose to about 58°. He has, however, given no explanation of what takes place, but merely stated that the stearine does not become fluid. His reasons for this conclusion consisted in the fact, that a thin layer of stearine did not change its form, although it became transparent when plunged into water at 52°. In repeating the experiment, I have found that, whenever the stearine becomes entirely transparent, it takes the form that would be assumed by a fused mass of any other substance.

stearine had therefore, by melting and again solidifying at 53·6°, passed into a different isomeric modification. The only evident difference between these two modifications is, that one melts immediately above its solidifying point, the other only at 12·2° above it, and that the former approaches slightly more to translucency, and is more reflective of light than the latter.

Before melting and solidifying at 53·6°, the stearine had the property of melting at that and even at lower temperatures, so low, that when we take the consequences, instead of the actual appearance, as evidence, we must admit that the proper point for placing the first melting point at is as nearly identical with the point at which it solidifies, after being heated 4° above its hitherto known melting point, as the melting point of any metal is with its solidifying point. What I mean by taking the consequences as evidence is, that the appearance of melting at 53·6° being succeeded by the transition into a modification which melts only at 63°, if we find that this transition is a consequence of keeping it a sufficient length of time at 51°, then, although we may see no appearance of melting, we must consider that it does melt at that temperature. In the case of this specimen, which melted at 63°, and solidified about 50·5°, it was found that although a temperature of 51° required a long time to produce the change into the modification melting at 63°, it was yet sufficient to do so, and for that reason I conclude that the first melting point is at least within 0·5° of the solidifying point. A reason why this transition at the lowest sufficient temperature is not preceded by the appearance of melting, consists in the fact "that next to water, fat possesses the greatest capacity for heat;"[*] and "is also one of the worst conductors of heat when fluid;"[†] so, that, after the heat of the water in the experiment has melted the surface of the bead, the surface, or say the superficial stratum, will have again solidified in the modified state before the heat has penetrated to the next interior stratum; hence, at the lowest temperature sufficient to produce the change, a portion is always in one or other solid state, and at no one moment is the whole transparent, but only different portions in successive moments.

It will be readily perceived that the temperature of the first melting point is dependent on that of the solidifying point (the solidifying point after heating 4° above the second melting point). As all temperatures above the solidifying point, and below the second melting point produce the modification of higher melting point, if the

* Lehmann's Phys. Ch. translated for Cavendish Soc. by Day, I, 261.
† Id. p. 260.

solidifying point was higher than it is, the first melting point must also have been higher, or it could not have existed at all.

It yet remained to be found what was the cause that, when the temperature had not been raised 4° above the second melting point, solidification set in before the temperature fell 12·2° below this melting point.

This depended on the fact that there was yet another melting point, and another isomeric condition corresponding to it.

When the temperature was raised only 1° or 2° above the second melting point, and then allowed to fall slowly 1° or 2° below it, solidification commenced, and proceeded, not suddenly, as at the ordinary solidifying point, but slowly, and when complete, the appearance of the fat was entirely different from what it had been in either of the foregoing modifications, it was more opaque and friable, and melted only at 66·5°, or 3·5° above its ordinarily known melting point.

To distinguish these different modifications, they will be called in the order of their melting points, the first, second and third; that melting at 51°, the first modification; that melting at 63°, the second; that melting at 66·5°, the third. The latter may be also called the crystalline condition, for it really is so; and what is very remarkable, as well from its connexion with the other facts in this paper, as from its having so long escaped observation, the crystals from ether have the third melting point only.

From what has been said it will be observed, that both the second and third modifications are producible in the interval between the first and second melting points; the second modification in the lower extremity of this interval, the third in the higher. There is, however, no particular point in this interval forming a marked boundary by which the two ranges of temperature that produce the two different modifications are separated. In the case of the specimen taken for illustration, and having its melting points respectively at 51°, 63°, and 66·5°, the second modification was alone producible under 56°, at least within any moderate time; at 56·5° a mixture seemed to be the result, whilst at 57°, and all temperatures between that and the third melting point, the third modification alone was produced.

It may also be collected from what has been stated, that neither the second nor third modification can be produced from a substance which has been heated to the third melting point; for the liquid which is then formed, solidifies only when the temperature falls below the first melting point, and is then necessarily in the first modification, unless after the lapse of hours.

What has been said of the specimen hitherto spoken of, may be summed up by saying that it has three melting points; it melts at the temperature of the first, solidifies; melts at the temperature of the second, solidifies; melts at the temperature of the third, and then solidifies only when the temperature has fallen below all three; and after solidifying here, it may be made to melt again at the first, at the second, and at the third melting points respectively, solidifying, as before, below all three; and these changes are producible in this succession to any extent without the slightest loss or gain of weight.

In specimens where the impurities predominate, as those having their second melting point at 61°, or below it, the third modification is procurable only by obtaining crystals from ether or some other solvent.

On the other hand, as the stearine approached to purity, the appearance of the second melting point subsided, insomuch that when a substance having its first melting point at 52°, and its third at at 69°·7, was obtained, it did not, on being heated continuously from the first to the third melting point, become fluid at any intermediate temperature; however, when it was melted at or near its first melting point, and allowed to solidify at the same temperature, and then suddenly removed to a temperature which by inference was judged to be a little above its second melting point, as 65°·5, it did melt.

At the same time that the second melting point was thus disappearing, the highest temperature for producing the second modification, instead of rising along with the melting points, was approaching more and more nearly to the first melting point, thus narrowing the limits for the production of the second modification and extending those of the third, so that in the specimen having its first and third melting points at 52° and 69·7° respectively, the highest temperature for producing the second modification was about 55°, or 3° above the first melting point, while in the less pure substance, having its first melting point at 51°, the corresponding point was 56°, or 5° above its first melting point.

These facts, along with the melting point, specific gravity, and external appearance* of the second modification being intermediate between those of the other two, lead to the inference that if stearine were obtained quite pure, the highest temperature at which the second modification would be producible would coincide with the first melting point; and there being consequently no range of temperature for producing the second modification, there would be no second modifi-

* Although the appearance is intermediate, it is quite distinct. It is described further on.

cation and no second melting point, but only a first and third melting point, or in that case, a first and second melting point; and that what I have called the second modification is a mixture of the other two modifications, owing its existence, somehow or other, to the impurities. But even were we certain that this were the case, there would still remain the difficulty of explaining how they could produce it. The following seems to me also a strong reason for believing it not a mixture. In the assumption that it is such, is implied that the relative quantities of the first and third modifications in it are such that when the melting point of the former is exceeded, its solvent action on the latter is sufficient to make the whole melt some distance below the third melting point. Now if this were correct, we ought, by increasing the proportion of the first modification, or, in other words, of the solvent, to be able to depress the melting point of the whole still more. But experiment showed that when a bead of substance having its second melting point at 63° was brought into the second modification by being melted and allowed to solidify at a little above its first melting point, it became limpid at the same temperature, 63°, as it did when it was allowed to solidify, only very partially, or when after solidifying, the greater part of it was again reduced to the first modification.

Dr. Hittorf* has lately shown in an interesting paper on selenium, that this substance has two allotropic modifications and two melting points to correspond; and that, after melting at the higher of the two, it solidifies only when the temperature has fallen considerably below both. Now it is also known that selenium softens considerably below what he calls its first melting point; but whether the changes which accompany this softening are those consequent upon a real fusion, has not been investigated; but should they be found to be such, there would be the closest analogy between its characters and those of stearine.

The following is a short table of the melting-point of mutton stearine at different stages of the purification:

No. of crystallizations.	Solidifying Points.	Melting Points.		
		1.	2.	3.
5	49°	49·5°	61·3°	64°
17	50·5	51	63	66·5
32	51·7	52	64·2(?)	69·7

From this table, it will be observed that the second melting point

* Pogg. Ann. LXXXIV, 214.

rises much more quickly than the first, with the removal of the impurities, and the third still more quickly than either of the other two. This is explained by what we know to be the general action of solvents; for the influence of the impurities is a solvent one, or in other words, one which tends to depress the melting point; and for any given quantity of impurities, this is greater at the temperature of the higher than of the lower melting point, so that this quantity of impurities being removed, the higher melting point rises in consequence more than the lower. The different modifications have probably also different solubilities, even at the same temperature; indeed, the fact of the third modification being always deposited from ether, whatever modification may have been dissolved, shows that it is the one most insoluble in ether. The property in question should, therefore, be ascribed in part to each of these causes.

Considering that in general an increase of specific gravity corresponds to a loss of latent heat, and that doubtless these different modifications of stearine depend on differences of latent heat, it became an object to take their specific gravities with as much precision as possible.*

The following table shows a decided difference in the density of the different modifications. Where two observations on the same substance at the same temperature are given, they were made on different quantities in different bottles as a test of the method. Whatever tem-

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* As there are other instances where the method employed might be used with some advantage, a description of it may be useful. A portion of dry stearine was put into a dry stoppered specific gravity bottle and weighed. The bottle was then filled with distilled water, inverted in a beaker containing distilled water, and the whole heated to 100°: in this way the fat melted, and allowed any adhering air, as well as that expelled from the water, to collect in a single globule; after cooling, the bottle was taken out of the beaker, and being placed in its ordinary standing position, the greater part of the globule of air rose into the neck of the bottle, whence it was expelled by filling its place with water. To remove the air which still adhered to the fat, a tube about two inches long, and wide enough to admit the head of the stopper, was attached by a piece of vulcanized caoutchouc tubing to the neck of the bottle, and filled with distilled water. The temperature of the water being about 30° degrees, the apparatus was placed in a beaker, under the receiver of the air-pump. On exhaustion, the remaining air in the bottle rose, by its elastic force, through the orifice in the stopper and through the water in the little reservoir. On readmission of the air to the receiver, the water in the reservoir was forced into the bottle to supply the place of the removed air. The bottle being thus filled was, after removal of the tube, again placed on its side, and the orifice immersed in a beaker of distilled water; by bringing the temperature of the water in the beaker to the required point, that in the bottle was brought to the same, and all the different modifications of the fat successively produced. Before taking the bottle out to weigh it, it is necessary to keep the temperature a considerable time at the point to which the determination refers, otherwise the slow cooling of the fat, arising from its great specific heat and bad conducting power, will occasion serious errors.

perature the determination is referred to, water at the same tempera-
ture is the unit.

SPECIFIC GRAVITIES.

3rd M.P. of substance.	Temp. at which determination was made.	Modifications.			
		1.	2.	3.	Fluid.
65°	15°	0·9872	—	—	—
66·5	15	0·9877	—	—	—
	15	0·9867	1·0101	1·0178	—
	15	—	—	1·0179	—
69·7	51·5	0·9600	—	1.0090	
	65·5	—	—	0·9931	0·9245
	68·2	—	—	0·9746	—

The volumes corresponding to these densities are as follows :

3rd M.P. of substance.	Temp. at which determination was made.	Modifications.			
		1.	2.	3.	Fluid.
65°	15°	1·0129	—	—	—
66·5	15	1·0124	—	—	—
	15	1.0134	0·9900	0·9825	—
	15	—	—	0·9824	—
69·7	51·5	1·0416	—	0·9910	
	65·5	—	—	1·0069	1·0816
	68·2	—	—	1·0260	—

From these tables it may be seen that the density does not change
sensibly with the condition of purity; that the third modification is
denser than the second; the second than the first; and, as might be
supposed, that the fluid modification is less dense than any of the
others; that the first and third, at least, although solids, expand much
more rapidly with increase of temperature than does water, a property
long known of the liquid fats, but not previously determined, I
believe, for any solid fat; that between 15° and 51·5°, the first modifi-
cation expands more than the third; it is however to be remarked,
that at the higher extremity of this interval, the first modification
approaches its melting point, which probably influences its rate of ex-
pansion.   We also observe, that within the range of 2·7° between the
temperatures 65·6° and 68·2° the third modification expands 0·0191
parts more than water; within the range of 14⁰ between the tempera-
tures 51·5⁰ and 65·5⁰, it expands only 0·0159 parts more than water;
while within the range of 36·5⁰, between the temperatures 15⁰ and
51·5⁰, it expands only 0·0086 parts more than water.

There can be no doubt that a greater number of these data taken

by the more convenient and exact method of a volumenometer, would point out some interesting relations.

None of these modifications conduct electricity. When a small portion of any of them formed part of the circuit of a very intense current produced by a powerful induced magnet with three Daniell's cells, the galvanometer was not sensibly deflected.

Not the least interesting fact, however, is that this property of existing in three modifications is not peculiar to stearine from mutton fat; it is possessed by many other fats.

At the same time that I prepared stearine from mutton fat, I also sought it in beef fat with the view of submitting to investigation the question of the constitution of the glycerine fats in general, as regards their products on saponification, by a method proposed to me by Dr. Williamson. The results of this investigation are reserved for a future communication.

Artzbächer* seems the only chemist besides Chevreul who has attempted to prepare stearine from beef fat. The stearine obtained by him from it melted at $60 \cdot 6°$.

Commencing with the same quantity of it as of the mutton fat, viz., two kilogrammes, I obtained, after eighteen crystallisations from ether, not more than a gramme of substance melting at $63°$; the quantity being now so small, it was useless to pursue the purification further, although the melting point of the residue in the mother-liquor, after removal of a second crop of crystals, was $2 \cdot 8°$ below that of the first crop. It possessed, however, all the properties of mutton stearine of the same degree of purity, so that $63°$ was only its second melting point.

A substance which is probably a vegetable tallow, but of whose history I know little, has also been the subject of investigation. In its crude state, it is of a pale yellow, cheese-like appearance, somewhat motley from parts of it being crystalline and others waxy; it has a slightly disagreeable smell. On saponification, it yields a dirty white soap which forms a brown solution, and on decomposition by strong acid, liberates an acid of a deep brown colour.

After one crystallisation of this substance from alcohol, and five from ether, there remained a glycerine fat, which melted only $1 \cdot 2°$ higher than the residue in the mother-liquor, so that it is not difficult to purify. Its properties were then analogous to those of stearine, but like the purer stearine, it does not, on being heated continuously from its first to its third melting point, viz., from $45 \cdot 6°$ to $64 \cdot 5°$, melt at any intermediate temperature, but when the temperature comes to $62°$, its appearance quickly changes from waxy to crystalline;

* Ann. Ch. Pharm. LXXX, 239.   Compt. Rend. trav. chim. 1849, 343.

this, and the results of some experiments similar to those by which the existence of the second modification was shown in stearine after its second melting point had disappeared, make me believe that this substance really has a second melting point at 62°. After melting at the third melting point, it solidifies in less time than does stearine above the first melting point; so that in order to bring it into the first modification, it must be cooled somewhat quickly, in less than an hour at most; but at whatever temperature it solidifies, it has the same properties as if it had been melted as well as solidified at that temperature. This is universally the case; the properties of the solid fat are regulated by the temperature at its own formation, not by that at which the antecedent liquid may have been formed.

The corresponding modifications of this substance, of mutton-stearine and of beef-stearine have the same appearance under the microscope. There is not much to be said of the first modification, unless that it appears as mamillæ radiated like hematite; when watched under the microscope, these mamillæ are seen to form suddenly when the temperature falls to the solidifying point; the second modification has an exfoliated appearance, somewhat suggestive of incipient crystallisation; the third is perfectly crystalline, and by proper attention, particularly in the case of the vegetable fat, the crystals can be obtained in the dry way as definite in form, as from ether, but smaller. So far as the eye can judge without means of measurement, the crystals of these three substances seem isomorphous, but I regret I have not been able to measure their angles.

Palmitine, from palm oil, after twelve or thirteen crystallisations from ether, margarine from butter, and also margarine from human fat, or at least the more solid portion of that substance after two crystallisations from alcohol, and one from ether, exhibited similar phenomena with respect to variety of modification and melting point.

On the other hand, neither elaidine, cocinine, nor any other of the substances in the subjoined table, has the property of existing in more than one modification.

In seeking for some feature in the constitution of the substances that have this property, which would separate them from those that have not, the attention is arrested by the fact, that most of the substances which possess it, as stearine, palmitine, margarine, are unquestionably the glycerine-fats, corresponding to certain members of the series of acids of the formula $(CH)_{2n} O_4$, while among those substances which do not possess it, there is not one, unless we except cocinine, which has such a constitution. In reference to cocinine, I may

observe, that although St. Evre's* analysis of cocinic acid agrees with the formula $C_{22} H_{22} O_4$, yet he, as well as Bromeis† describe it as destitute of one character, crystallisation and opacity on cooling, which, so far as is known, belongs to every other member of the series of acids to which his formula assigns it.

In the following table, instead of the formula of the fats themselves, are written those of the acids derivable from them; for as yet considerable doubt must exist as to those of the fats. In the other cases the formulæ of the substances themselves are written.

	Formulæ.	Solidifying Points.	Melting Points.		
			1.	2.	3.
Mutton-stearine	$C_{34} H_{34} O_4$	51·7°	52·0°	64·2°?	69·7°
Beef-stearine	$C_{34} H_{34} O_4$	50·5	51·0	63.0	67·0
Substance from vegetable tallow	—	45·0	45·6	62·0	64·5
Palmitine from palm oil . . .	$C_{32} H_{32} O_4$	45·5	46·0	61·7	62·8
Margarine from butter . . .	$C_{34} H_{34} O_4$	40·0	40·5	51·0	52·6
Margarine (?) from human fat .	—	43·5	44·2	54.5	56·0
Cocinine	$C_{22} H_{22} O_4$	29·3	33.5		
Elaidine‡	$C_{36} H_{34} O_4 \left\{ \begin{array}{l} 23\cdot7 \\ 28\cdot0 \end{array} \right.$		38·0		
Stearic acid	$C_{34} H_{34} O_4$	65·8	68·0		
Palmitic acid	$C_{32} H_{32} O_4$	59·0	61·0		
Margaric acid from butter . .	$C_{34} H_{34} O_4$	50·5	52·3		
Stearic ether	$C_{38} H_{38} O_4$	33·0	33·7		
Cerotic ether§	$C_{58} H_{58} O_4$	60·0	60·3		
Cerotin (alcohol)	$C_{54} H_{56} O_2$	81·0	81·0		
Cerotene	$C_{54} H_{54}$	57·0	57·8°		
Chinese wax	$C_{108} H_{108} O_4$	80·5	81·0		
Paraffin	$(CH)_{2n}$	43·5	43·5		

XIX.—On the qualitative separation of Arsenic, Tin, and Antimony,

By Geo. F. Ansell.

Although a great many processes for the purposes mentioned have been suggested, processes which, in the hands of experienced chemists, will invariably give satisfactory results, a method is still wanted,

* Ann. Ch. Phys. [3], XX, 91.   Ann. Ch. Pharm. LXIV, 341.
† Ann. Ch. Pharm. XXXV, 277.
‡ The solidifying point of elaidine is precarious.
§ I am indebted to the kindness of Mr. Brodie for the specimens upon which I operated of the five last-mentioned substances.

sufficiently simple and precise, to admit of being used by the beginner in analytical chemistry. At the suggestion, and under the direction of Dr. Hofmann, I have made a series of experiments upon this subject, and now beg to submit the result to the Chemical Society. The precipitates produced by sulphuretted hydrogen are heated with sulphide of ammonium in the usual way, and the sulphide of ammonium solution reprecipitated with hydrochloric acid and hydrosulphuric acid.

The precipitate thus obtained, which may consist of bisulphide of tin, pentasulphide of arsenic and pentasulphide of antimony, and occasionally of the sulphides of gold and platinum, is redissolved in nitrohydrochloric acid, and the solution poured into an ordinary apparatus for generating hydrogen gas, so arranged as to allow of washing the gas with a dilute solution of acetate of lead, which absorbs any hydrochloric acid or sulphuretted hydrogen, and to pass the mixture of antimoniuretted and arseniuretted and free hydrogen into a test-tube half-filled with pure concentrated nitric acid.

If the gas be passed moderately slowly, the whole of the metallic hydrides are decomposed; water, arsenic acid and antimonic acid being formed. The nitric acid solution obtained after the gaseous mixture has passed for about a quarter of an hour, is evaporated; and the residue, after being exposed to a tolerable heat upon a sand-bath, in order to expel the last traces of nitric acid—which is an essential condition of success, inasmuch as antimonic acid is slightly soluble in water containing nitric acid—contains antimonic acid, arsenic acid and arsenious acid.

The residue is now exhausted with warm water, which takes up all the arsenic and arsenious acid. The aqueous solution, when mixed with nitrate of silver and neutralized drop by drop with ammonia, yields, if arsenic be present, a precipitate of arseniate or arsenite of silver. The colour of this precipitate varies to a considerable extent : if the quantity of arsenic be considerable, it presents the pure red of the arseniate of silver; but when the quantity of arsenic is minute in proportion to the amount of antimony, the heat necessary to expel the last traces of nitric acid, reduces part of the arsenic acid to the state of arsenious acid, the silver-salt of which imparts a yellow tint to the precipitate produced by nitrate of silver and ammonia. This change of colour in the precipitate is an inconvenience, but it does not materially affect the value of the method ; since, in a carefully conducted operation, the formation of any precipitate whatever indicates the presence of arsenic.

The residue which is left after complete exhaustion with water is antimonic acid. It is dissolved in the smallest amount of nitro-

hydrochloric acid; in the ordinary analysis, the quantities are frequently so minute that it is advisable to boil filter and all in aqua regia; the excess of acid is evaporated as far as possible, and the remaining solution is mixed with sulphuretted hydrogen water. If a trace of antimony be present, the liquid at once assumes an orange-yellow colour, and on boiling, decidedly orange-yellow flakes are separated.

The method was repeatedly tried by myself and by several of my fellow-pupils, with mixtures in which either one milligramme of arsenic was associated with ninety-nine milligrammes of antimony, or *vice versâ*, one of antimony with ninety-nine of arsenic. Both arsenic and antimony could be detected without difficulty if the operations were carried out with the necessary precautions.

The detection of tin presents no difficulty. The whole of this metal remains in the apparatus for generating hydrogen, either in the form of protochloride, or in the shape of a finely-divided metallic precipitate. If the quantity of tin is considerable, it is sufficient to filter the liquid in the apparatus, and to add to the filtrate protochloride of mercury. A white precipitate of subchloride of mercury indicates the presence of tin. Should this experiment yield no result, the metallic precipitate (tin with a portion of antimony and arsenic) is detached from the plates of zinc, and dissolved in hydrochloric acid, and the solution tested by protochloride of mercury.

It need scarcely be mentioned, that both the sulphuric acid and the zinc used in this operation must be perfectly free from arsenic, tin and antimony.

Note.—This operation is more successful if the nitric acid be kept hot during the time that the gases are passing, but this is not by any means necessary.*

If antimony be present, the nitric acid will soon become opaque, and after a few minutes deposit a white precipitate.

* Mr. Ansell's mode of testing, which is particularly calculated for small quantities of antimony, may be conveniently combined with an additional experiment for arsenic. Incredibly minute quantities of the latter element, even in the presence of a very large amount of antimony, are *readily* and *infallibly* recognized by passing the mixture of antimoniuretted and arseniuretted hydrogen into nitrate of silver. As is well known, the whole of the antimony is precipitated in the form of antimonide of silver (Sb Ag₃), while every trace of arsenic remains in solution, in the form of arsenious acid. On neutralizing the liberated nitric acid by ammonia, the characteristic yellow arsenite of silver is precipitated. If the gas has been passed for a long time, the solution is sometimes free from silver. In this case, the silver precipitate of course appears only after the addition of a drop of nitrate of silver.

The separation of the antimony from the black precipitate, which is a mixture of metallic silver and antimonide of silver, is attended with difficulties; and I find it more convenient to use Mr. Ansell's method for the detection of minute quantities of antimony.—A. W. H.

XX.—*Observations upon a new series of Double Chlorides containing Diplatosammonium.*

By G. B. Buckton, F.L.S.

The consideration of the action of cyanogen upon diplatosamine, communicated on a former occasion, has induced me to undertake some experiments with a view to the preparation of that base in combination with cyanic acid. In the course of this examination, I have been led to the discovery of a new series of double salts, which appear to offer some interest. A description of these salts, together with some remarks upon chloride of diplatosammonium with chromic acid, forms the subject of the present paper.

CHLORIDE OF DIPLATOSAMMONIUM AND CHLORIDE OF LEAD.

My attention was first directed to the white crystalline precipitate which falls abundantly on mixing concentrated solutions of chloride of diplatosammonium with acetate or nitrate of lead. After washing the mass, it was dissolved in boiling water and filtered whilst hot. The substance reappeared on cooling, in the form of small quadrilateral plates of a pearly lustre, which often were sufficiently thin to reflect the colours of the soap-bubble. When gathered on a filter, they appeared as a mass of frosted silver, and the dry crystals resembled those of cholesterine.

As this substance did not decompose at a heat below 170° C., the portions set apart for analysis were all dried at a temperature between 110° and 120°.

> I.   0·5948 gms. of substance gave
>   0·5612 ,, ,, chloride of silver, equal to
>   0·1388 ,, ,, chlorine.
> II.   0·5308 ,, ,, substance gave
>   0·5006 ,, ,, chloride of silver
>   0·1238 ,, ,, chlorine.
> III.   0·5700 ,, ,, substance gave
>   0·5326 ,, ,, chloride of silver
>   0·1317 ,, ,, chlorine.
> IV.   0·6042 ,, ,, substance gave
>   0·2976 ,, ,, sulphate of lead, equal to
>   0·2033 ,, ,, lead. The filtrate by ignition gave
>   0·1974 ,, ,, platinum.

V. 0·6648 gms. of substance gave
   0·3271 „ „ sulphate of lead
   0·2235 „ „ lead.
VI. 0·7586 „ „ substance burnt with oxide of copper
   0·1456 „ „ water, equal to
   0·0161 „ „ hydrogen.
VII. 0·7530 „ „ substance, with soda lime, gave
   1·0820 „ „ platino-chloride of ammonium, or
   0·0678 „ „ nitrogen.

From which numbers the following per-centages are calculated:

	I.	II.	III.	IV.	V.	VI.	VII.
Chlorine	23·34	23·32	23·10	—	—	—	—
Lead	—	—	—	33·48	33·62	—	—
Platinum	—	—	—	32·67	—	—	—
Hydrogen	—	—	—	—	—	2·13	—
Nitrogen	—	—	—	—	—	—	9·0

which correspond to the formula:

$$\text{Pt H}_6 \text{ N}_2 \text{ Cl . Pb Cl.}$$
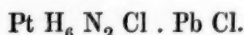
The theoretical and experimental per-centages are as follows:

	Theory,		Experimental mean.
Pt	99·00	32·19	32·67
H$_6$	6·00	1·95	2·13
N$_2$	28·00	9·10	9·00
Pb	103·56	33·67	33·55
Cl$_2$	71·00	23·15	23·25
	307·56	100·00	100·60

This substance is insoluble in alcohol, and also in hydrochloric acid. Concentrated sulphuric acid freely liberates fumes of hydrochloric acid, sulphate of lead being thrown down. Hydrosulphuric acid isolates chloride of diplatosammonium, with evolution of hydrochloric acid and precipitation of sulphate of lead, which, however, always carries down a portion of platinum, and renders it necessary to estimate the lead in the above analysis as sulphate, by adding sulphate of ammonia and free sulphuric acid.

A convenient method of preparing this salt, presented itself as a matter of course in the direct union of the two chlorides, the combination being promoted by adding hydrochloric acid, which facilitates also the regular crystallisation.

In the case of precipitation by acetate of lead, as might have been foreseen, the mother-liquor yielded on concentration, crystals of acetate of diplatosamine, to identify which, the substance was converted into chloride by adding hydrochloric acid, evaporated to dryness, and after solution in water, precipitated by alcohol. The platinum obtained by ignition left no doubt of the composition of this salt.*

The deportment of chloride of diplatosammonium with chloride of lead, induced me to study several other double compounds of this substance.

CHLORIDE OF DIPLATOSAMMONIUM AND PROTOCHLORIDE OF MERCURY.

This substance falls as a bulky crystalline salt, which is easily soluble in boiling water, from which, after filtration, it recrystallises in plumose groups composed of a multitude of cubes. The solution, when rapidly cooled, yields nacreous plates, not unlike those of the lead-salt. This substance, like all those hereafter described, produces more regular forms from an acid than from a neutral solution; and its insolubility in hydrochloric acid may be seen by its addition causing a partial precipitation in the saturated aqueous solution.

> I.   0·6574 gms. of salt dried at 120°, gave on ignition
>   0·2130 ,,   ,, platinum.
> II.   0·5022 ,,   ,, salt gave
>   0·1640 ,,   ,, platinum.
> III.   0·5156 ,,   ,, salt gave
>   0·4874 ,,   ,, chloride of silver, equal to
>   0·1205 ,,   ,, chlorine.
> IV.   0·5196 ,,   ,, salt gave
>   0·4880 ,,   ,, chloride of silver
>   0·1207 ,,   ,, chlorine.

From these numbers the following per-centages are deduced :

	I.	II.	III.	IV.
Platinum	32·49	32·65	—	—
Chlorine	—	—	23·37	23·23

---

* 0·4050 gms. of substance gave
    0·2838 ,,   ,, platinum.
The theoretical and experimental per centages are for,
$$Pt\ H_6\ N_2\ Cl$$

	Theory.	Experiment.
Platinum	58·75	58·51

which are in accordance with the formula :

$$Pt\ H_6\ N_2\ Cl.\ Hg\ Cl.$$
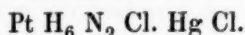
The numbers required by theory and obtained by experiment are annexed for comparison.

			Theory.		Experimental mean.
Pt	.	.	99·0	32·58	32·57
H_6	.	.	6·0	1·97	—
N_2	.	.	28·0	9·21	—
Hg	.	.	100·0	32·89	—
Cl_2	.	.	71·0	23·35	23·30
			304·0	100·00	

This compound bears a considerable temperature without decomposition. At a certain point it fuses, emitting dense fumes of chloride of ammonium and chloride of mercury. The residue, after ignition, consists of a compact foil of pure platinum, which lines the vessel in which the operation is made.

CHLORIDE OF DIPLATOSAMMONIUM AND SESQUICHLORIDE OF IRON.

The union of these solutions does not result in the formation of a double chloride; but a yellowish granular substance is deposited, nearly insoluble in water and in ammonia. This salt yields a yellow solution with caustic potash, from which it is again thrown down by addition of hydrochloric acid. The potash solution liberates ammonia on boiling, and the dry salt disengages hydrochloric acid when treated with sulphuric acid.

   I.   0·3978 gms. of substance, dried at 110° gave on ignition
       0·1922 ,, ,, platinum.
  II.   0·3970 ,, ,, substance gave
       0·1930 ,, ,, platinum,

corresponding to the per-centages :

	I.	II.
Platinum . .	48·31	48·61

This salt is therefore the chloride of Gros' radical

$$Pt\ Cl\ H_6\ N_2\ .\ Cl,$$
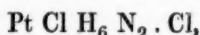
which requires the following theoretical numbers.

	Theory.	Mean of Experiment.
Platinum . . .	48·41	48·46

After precipitation of the iron solution by an excess of the platinum-salt, it will no longer strike a black colour with tincture of galls ; and ferrocyanide of potassium also throws down a nearly colourless precipitate, thus proving that the iron has been reduced from the sesquichloride to the protochloride, the disengaged equivalent of chlorine having united itself to the platinum-chloride thus :

$$Pt\ H_6\ N_2\ Cl\ +\ Fe_2\ Cl_3\ =\ Pt\ Cl\ H_6\ N_2,\ Cl\ +2\ (Fe\ Cl)$$
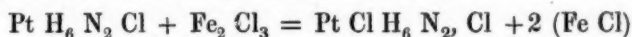
The salts of protoxide of iron do not appear to be acted upon chloride of diplatosammonium.

CHLORIDE OF DIPLATOSAMMONIUM AND CHLORIDE OF ZINC.

On mixing the concentrated solutions, a very soluble salt falls, which may be recrystallised in colourless plates, possessing the general characters of the substances previously described. It may be conveniently purified by precipitation from the aqueous solution by alcohol, and after drying the mass, reproducing the crystals from boiling water. This substance was dried at 110°, and gently heated with carbonate of soda. After washing the mass with water, it was digested with sulphuric acid, and the platinum-black produced was ignited and weighed.

> I.   0·6562 gms. of substance gave
>   0·2734 ,, ,, platinum.
> II. 0·5176 ,, ,, substance
>   0·6282 ,, ,, chloride of silver, or
>   0·1554 ,, ,, chlorine.

The calculated per-centages are for :

	I.	II.
Platinum	41·66	—
Chlorine	—	30·02

which agree with the formula

$$Pt\ H_6\ N_2\ Cl\ .\ Zn\ Cl.$$
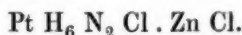
The theoretical and experimental numbers for 100 parts are :

	Theory.		Experiment.
Pt	99·00	41·86	41·66
H_6	6·00	2·54	—
N_2	28·00	11·84	—
Zn	32·52	13·74	—
Cl_2	71·00	30·02	30·02
	236·52	100·00	

CHLORIDE OF DIPLATOSAMMONIUM AND CHLORIDE OF COPPER.

This double compound is immediately formed on mixing the two concentrated solutions. After washing the precipitate from the copper-salt, which should be in slight excess, and drying it at 100°, it has a beautiful olive-green colour, and is composed of yellow plates possessing a metallic lustre. As this salt is decomposed by boiling water, it cannot be purified by recrystallisation, which perhaps may be taken as some apology for the following numbers, which are only approximative, yet sufficiently near to establish the formula.

A weighed portion was gently ignited with carbonate of soda, until all ammonia was driven off; and after washing the mass, it was dissolved in nitrohydrochloric acid, concentrated, and then treated with chloride of ammonium and a large excess of alcohol. The platinum was determined by igniting the ammonio-bichloride obtained, and the copper was estimated from the filtrate by adding potash with the usual precautions.

I.   0·7600 gms. of substance gave
     0·3166   „   „ platinum, and
     0·1364   „   „ oxide of copper or
     0·1088   „   „ copper.
II. 0·6458   „   „ substance gave
     0·1126   „   „ oxide of copper or
     0·0898   „   „ copper.
III. 0·6948   „   „ substance gave
     0·2875   „   „ platinum.

The per-centages are:

	I.	II.	III.
Platinum	41·65	—	41·37
Copper	14·31	13·90	—

From which is deduced the formula:

$$Pt\ H_6\ N_2\ Cl\ .\ Cu\ Cl.$$
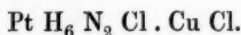
The theoretical and experimental numbers are:

		Theory.		Experimental mean.
Pt	. .	99·00	41·90	41·51
H$_6$	. .	6·00	2·54	—
N$_2$	. .	28·00	11·85	—
Cu	. .	31·66	13·41	14·10
Cl$_2$	. .	71·60	30·30	—
		236·26	100·00	

Previous to solution in water, the crystals of this substance become colourless, and on applying heat, a heavy granular salt is formed, which exibits all the reactions of Gros' chloride. The supernatant fluid, which becomes of a pale green hue, after sufficient concentration, is precipitated by alcohol in the form of greenish films, which may be regarded as the corresponding salt of the subchloride of copper and diplatosammonium, as an exactly similar substance results from the union of these bodies, a hydrochloric solution of the former being employed. The reaction therefore appears to be similar to that observed in the case of sesquichloride of iron. The change may be thus expressed in the form of an equation :*

$$2(\text{Pt } H_6 N_2 \text{ Cl . Cu Cl}) = \text{Pt } H_6 N_2 \text{ Cl . Cu}_2 \text{ Cl} + \text{Pt Cl } H_6 N_2 \text{ . Cl.}$$
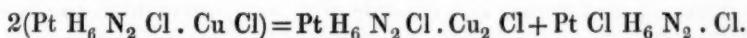
The double salt containing the chloride of copper is easily soluble in potash with which it forms an intense blue. It is decomposed by heat, with deposition of oxide of copper.

CHLORIDE OF DIPLATOSAMMONIUM AND PROTOCHLORIDE OF TIN.

On adding an acid solution of the latter to the platinum-salt, a white voluminous precipitate falls, which is easily dissolved by heat ; and the solution again deposits delicate films on standing, which possess the external character of the compounds previously described. The crystals, however, in this case, are always more or less coloured by binoxide of tin.

This decomposition is hastened by heating the solution, which turns to a deep port-wine red colour, and deposits a powder composed of reduced platinum and binoxide of tin, chloride of ammonium being formed at the same time.

CHLORIDE OF DIPLATOSAMMONIUM AND BICHLORIDE OF TIN

may be obtained in a dry state by precipitation in a strong acid solution, and subsequently washing the mass, first with hydrochloric acid and then with alcohol. From the difficulty in obtaining these salts of tin in a sufficient state of purity, no attempt was made to obtain a quantitative analysis.

Chloride of diplatosammonium and chloride of barium throw down from their saturated solutions a crystalline precipitate, which proved to be merely the latter salt, isolated by the difference of its affinity for water.

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* This equation probably does not express the whole reaction, as a secondary product may be obtained in small quantity from the filtrate in acicular groups.

Nitrate of suboxide of mercury does not form any double compound when added to chloride of diplatosammonium; and no union of chloride of silver with the latter substance could be effected, even when it was previously dissolved in ammonia.

BICHROMATE OF DIPLATOSAMINE.

Considering the well marked affinities of this base, I was curious to study its behaviour under the influence of chromic acid, thinking it not improbable that an interesting product of oxidation might arise from the action.

Chromic acid forms, with chloride of diplatosammonium, an abundant yellow precipitate, sparingly soluble in cold water, and resembling chromate of lead. From a hot solution it is deposited in minute cubic grains, which are insoluble in alcohol, and appear to be unaffected by dilute sulphuric acid. They do not contain chlorine; but hydrochloric acid is found in the filtrate, after precipitation of the yellow salt.

For analysis, advantage was taken of the peculiar action of alcohol and hydrochloric acid upon the solution of this substance, which in boiling is resolved into sesquichloride of chromium, aldehyde, and a crystalline substance, which proved to be the chloride of Gros' radical.*

As the substance is slightly decomposed at 100°, the salt was dried *in vacuo*, dissolved in water, reduced by alcohol and hydrochloric acid, evaporated nearly to dryness, and seven or eight times the volume of alcohol added to render the platinum-salt insoluble. After standing, this salt was filtered off and ignited, and the sesquioxide of chromium subsequently precipitated from the filtrate by ammonia. In another instance, the chromic acid was precipitated by acetate of lead, and the platinum was obtained by igniting the salt in the filtrate.

I. 0·6366 gms of substance gave
    0·8443   „   „ chromate of lead equal to
    0·1451   „   „ chromium and
    0·2594   „   „ platinum.

---

* 0·5290 gms. of this substance gave, on ignition
    0·2566 „   „ platinum.

The chloride of Gros' salt (Pt Cl H_6 N_2. Cl) requires

	Theory.	Experiment.
Platinum	48·41	48·50

II. 0·5448 gms. of substance gave
    0·1776 „ „ sesquioxide of chromium or
    0·1238 „ „ chromium and
    0·2224 „ „ platinum.
III. 0·7498 „ „ substance produced
    0·2381 „ „ sesquioxide of chromium
    0·1669 „ „ chromium and
    0·3037 „ „ platinum.

The per-centage composition :

		I.	II.	III.
Chromium	.	22·79	22·72	22·26
Platinum	.	40·74	40·08	40·51

This substance is, therefore, the bichromate of diplatosamine, the formula of which is :

$$Pt\ H_6\ N_2O\ .\ 2Cr\ O_3.$$
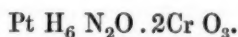
For comparison, the numbers required by theory and the mean by experiment are subjoined :

			Theory.		Experimental mean.
Pt	.	.	99·0	40·35	40·44
H_6	.	.	6·0	2·44	—
N_2	.	.	28·0	11·41	—
Cr_2	.	.	56·3	22·95	22·59
O_7	.	.	56·0	22·85	—
			245·3	100·00	

From these numbers it appears that the salt is anhydrous, and so far it has the anomalous constitution of the corresponding potash and ammonia compounds. The decomposition effected by alcohol and hydrochloric acid is represented by the following equation :

$$Pt\ H_6\ N_2\ O\ .\ 2\ CrO_3 + C_4\ H_5\ O\ .\ HO + 5\ H\ Cl =$$
$$Pt\ Cl\ H_6\ N_2\ .\ Cl + Cr_2\ Cl_3 + C_4\ H_4\ O_2 + 7\ HO.$$
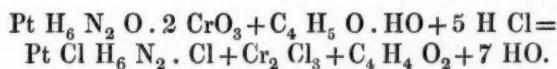
I have failed in obtaining more than two-thirds of the calculated nitrogen by igniting the substance with soda-lime; and no increase was observed by addition of a small quantity of sugar previous to burning. An explanation is found in the fact, that pure nitrogen is energetically liberated when the salt is gently heated. The decomposition is accompanied with scintillation, and the products are a black powder composed of platinum and sesquioxide of chromium,

nitrogen, water, and ammonia. The salt may also be kindled by live charcoal in a similar manner to gunpowder.

The following equation represents this reaction:

$$3 (Pt\ H_6\ N_2\ O\ .\ 2\ CrO_3) = Pt_3 + 3\ Cr_2\ O_3 + 2\ NH_3 + 12\ HO + 4\ N.$$
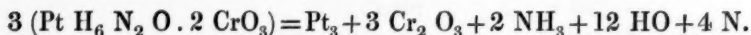
An exactly similar decomposition was first observed by Hayes in the bichromate of ammonia; and the subject has since been more fully investigated by Messrs. Richmond and Abel.

Monochromate of diplatosamine is formed on crystallising the bichromate from an ammoniacal solution, when it is sometimes deposited in pale yellow groups of crystals having the lustre of floss-silk; at other times it forms large cubical masses.

The analyses of this substance have not been very concordant; but nevertheless, the numbers are such as to leave little doubt of the formula being represented by $Pt\ H_6\ N_2\ O\ .\ Cr\ O_3$. The behaviour of this compound is similar to that of the bichromate, and like that salt, it is soluble in potash, which does not liberate ammonia until it is boiled.

From the foregoing remarks, it will be seen that chloride of diplatosammonium does not, in the generality of cases, follow the order of double decomposition; but that a direct combination of the two chlorides in the above-mentioned instances ensues, even when the precipitant does not happen itself to be a chloride. The platinum-radical has also a marked tendency to form these double compounds, as it appears to be immaterial whether sulphate of diplatosamine be employed to precipitate chloride of copper, or sulphate of copper be used with chloride of diplatosammonium.* The mercury-salts also seem to give the same result under like circumstances.

The composition of these double chlorides is satisfactorily borne out by the observation of Peyrone, that Magnus' green compound is immediately formed on mixing chloride of diplatosammonium with a hydrochloric solution of protochloride of platinum. Magnus' compound may be thus regarded as a binary salt of this series:

$$2 (Pt\ H_3\ N\ .\ Cl) = Pt\ H_6\ N_2\ Cl\ .\ Pt\ Cl.$$
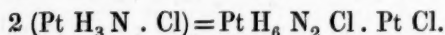
Reiset also has described and analysed the red (yellow?) compound containing the bichloride of platinum, the existence of which might have been foreseen after the existence of the above described bodies had been established.

* In this case, the precipitated salt is nearly colourless, unless a little free hydrochloric acid is present.

XXI.—*On the Acid Oxalates of the Earths.*

By Edward Clapton.

In the Annales de Chimie [2] LXXIII, 263, M. Berard describes a crystalline oxalate of baryta, which he found to contain 45·04 per cent of baryta, and accordingly viewed as consisting of the earth combined with twice the amount of oxalic acid contained in the neutral oxalate.

M. Darracq had also previously observed a binoxalate of baryta.*

A superoxalate of strontia, of doubtful composition, has since been described by Dr. Thompson.

There have been, however, more recently, some doubts cast upon the existence of superoxalates of this class of oxides; but the investigations about to be detailed show that they can easily be procured in a distinct and definite form.

ACID OXALATE OF BARYTA.

When about equal quantities of saturated solutions of oxalic acid and chloride of barium are mixed together, no cloudiness appears at first; but after the lapse of perhaps a minute, crystals begin to form, and presently they fall in abundance. The crystals are very acute rhomboidal plates; they are soluble in 336 parts of cold water at 60°, the solution reacting and tasting strongly acid; hot water decomposes them. When treated with a solution of ammonia, an oxalate of ammonia is formed, leaving behind oxalate of baryta. Potash acts similarly. The salt is not affected by alcohol or ether. After having been dried *in vacuo,* the salt loses nothing at 212° F., but by a heat of 350° F., water is given off; it loses oxalic acid at about 400° F. Subsequently it is converted into carbonate, with evolution of carbonic oxide.

In order to determine the composition of this salt, the following analyses were made:

I. 14·15 grs. of salt, dried *in vacuo,* were dissolved in dilute acid, and the baryta was precipitated by sulphuric acid. 9·8 grs. of sulphate of baryta were obtained.

II. 12·6 grs. of a different preparation similarly treated, gave 8·9 grs. of sulphate of baryta.

III. 22·41 grs. heated to redness, yielded 13·2 grs. of carbonate of baryta.

* Ann. Ch. Phys. [2] XL, 69.

These results give the following per-centage amounts of baryta:

	I.	II.	III.	Average.
Baryta	45·5	46·35	45·74	45·86

This accords well with the amount of baryta as calculated from the formula, $BaO . C_2 O_3 + HO . C_2 O_3 + HO$:

Baryta	.	.	45·98
Oxalic acid	.	.	43·22
Water	.	.	10·80
			100·00

The mere heating of the salt at given temperatures, so as to drive off its various constituents, did not give very accurate numerical results; the loss at 350° F. upon 22·41 grs. in an experiment of this character, was 1·61 instead of 1·21; at 400° F. it was 7·91. instead of 7·26.

An organic combustion of the salt was made. 12·75 grs. yielded 6·38 grs. of carbonic acid, and 1·6 grs. of water. The per-centage of carbonic acid is here 47·7, instead of 52·8, the loss being doubtless caused by the retention of some carbonic acid by the baryta in the tube. The amount of hydrogen in this, as also in another experiment, where 24·63 grs. yielded 3·15 grs. of water, little exceeds the calculated amount.

1st. Experiment.	2nd. Experiment.	Calculated.
1·39 per cent.	1·42 per cent.	1·2 per cent.

ACID OXALATE OF STRONTIA.

Upon mixing together strong solutions of oxalic acid and chloride of strontium, crystals presently fall, which are found to be of a mixed kind, presenting large rhomboidal crystals and small octahedra.

The general characters of the salt are similar to those of the acid baryta-salt.

When heated to 212°, many of the crystals became white in colour, and water was given off, having in some instances a slight acid reaction.

The following estimations of the base were made:

I. 18·45 grs. dried at 212° yielded 12·8 of carbonate of strontia.

II. 33·5 grs. of a different preparation yielded 21·45 grs. of the carbonate.

III. 19 grs. of a portion which had crystallized slowly from the solution, after the first crop of crystals had subsided, yielded 11·3 grs. of the carbonate.

IV. 10 grs. dried *in vacuo,* gave off 0·85 grs. of water at 212° F., and yielded 5·8 grs. of the carbonate.

V. 5·55 grs. of the salt prepared by recrystallising the acid oxalate from solution in hot oxalic acid, yielded 3·4 grs. of the carbonate.

These results are very discordant, giving respectively the following percentage amounts of strontia :

	I.	II.	III.	IV.	V.
Strontia . .	48·7	45	41·79	44·55*	43·2

The amount of strontia is, therefore, in every instance less than would be given by the neutral oxalate, viz., 49 per cent, but it exceeds that required by the formula $SrO . C_2 O_3 + HO . C_2 O_3 + HO$, viz. 36·6 per cent., or $SrO . C_2O_3 + HO . C_2O_3$, viz., 39·1 per cent. However, in the third experiment the discrepancy is small. In all probability, each sample of salt was a mixture of salts of different compositions ; but there can be no doubt whatever that they contained at least one acid oxalate of strontia.

<div align="center">LIME-SALT.</div>

An attempt was made to produce an acid oxalate of lime by similar means, but without success ; the precipitate which fell had the appearance of neutral oxalate of lime, and 6·15 grs. dried at 212° yielded 4 grs. of carbonate of lime ; the amount obtained from a substance of the formula $CaO . C_2 O_3 . HO$ would be 4·2 grs.

<div align="center">MAGNESIA-SALT.</div>

Very strong hot solutions of sulphate of magnesia and oxalic acid were mixed together. A white powder separated which was almost insoluble in water ; upon heating it, water was quickly driven off ; and by a red heat, it was found that 8·97 grs. yielded 2·69 grs. of magnesia, agreeing with the formula of the simple oxalate $MgO . C_2 O_3 . HO$, which would have given 2·82 grs.

Dr. Gladstone, who has kindly watched over the progress of this investigation, desires me to append the following remarks upon the theoretical bearing of these results :

"A principal point of interest connected with these acid salts, is the corroborative evidence they afford of the bibasic character of the contained acid.

"Oxalic acid may well be viewed as the first member of the series

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* Calculated as dried at 212°.

$C_n H_{n-1} O_4$, or (viewing them as bibasic) $C_n H_{n-1} O_8$. This series advances by the addition of multiples of the increment $C_2 H_2$: the superior members are succinic, adipic, pimelic, suberic, and sebacic acids. Pyrotartaric acid also has claims to be considered one of the same group. The properties common to these acids as well as oxalic acid, are their general production by the violent oxidation of organic substances; their resisting most methods of oxidation; their being solid and crystalline at ordinary temperatures; but capable of fusion and sublimation though partially decomposed if rapidly heated; and their tendency to form acid as well as neutral salts, and amidic acids as well as amides. Late investigations have tended to show that these acids should be considered bibasic; the arguments which have led to this conclusion apply equally to oxalic acid. The rational formula of the crystalline oxalate of baryta is, therefore,

$$Ba\, O \,.\, HO \,.\, C_4 O_6 + HO.$$

"The series formed by the above-mentioned hydrated acids is as follows:

Oxalic acid	. .	$C_4\ H_2\ O_8$
Succinic	. . .	$C_8\ H_6\ O_8$
Pyrotartaric	. .	$C_{10}\ H_8\ O_8$
Adipic .	. . .	$C_{12}\ H_{10}\ O_8$
Pimelic	. . .	$C_{14}\ H_{12}\ O_8$
Suberic	. . .	$C_{16}\ H_{14}\ O_8$
. . .	. . .	
Sebacic	. . .	$C_{20}\ H_{18}\ O_8$"

XXII.—*Researches on the Anhydrous Organic Acids,*

By Chas. Gerhardt.

(Continuation from a Letter to Dr. Williamson.)

In continuing the researches of which I had the honour of communicating the commencement to the Society, I have found a valuable reagent not yet used in organic chemistry, and extremely valuable for the preparation of various chlorides used in the formation of anhydrous acids. This reagent is the oxychloride of phosphorus, $PO\ Cl_3$, a liquid which effects the decomposition of a great number of salts as easily as it decomposes water, and enabled me, among other things, to prepare *Acetic chloride,*

$$C_2\ H_3\ O\ Cl,$$
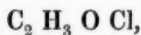
a colourless liquid, very mobile, and boiling at 56° C. It fumes slightly in the air, and is decomposed by water into acetic and hydro-chloric acids. With this new chloride, I have obtained several new active compounds by double decomposition.

I prepare *acetic benzoate* or *benzoic acetate* by the action of acetic chloride on dry benzoate of soda, $C_7 H_5 O_2$ Na. The reaction is very brisk, and is soon completed without the aid of external heat. The syrup produced, washed with water and carbonate of soda, leaves an oil heavier than water, neutral to test-paper, and possessing an agreeable odour of Spanish wine. This oil is easily purified from water and other foreign matters by agitation with ether free from alcohol; and after the ether has been removed by a gentle heat, the product shows by analysis, the composition:

$$C_9 H_8 O_3 = \left\{ \begin{matrix} C_2 & H_3 & O \\ C_7 & H_5 & O \end{matrix} \right\} O \; .$$
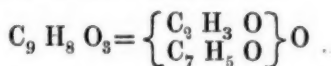
Boiling water renders it acid, but the complete decomposition requires a long action; and the intervention of alkalies is needed, as in the case of ethers. When subjected to distillation, acetic benzoate separates at about 150° into *anhydrous acetic acid* (*acetic acetate*) and *anhydrous benzoic acid* (*benzoic benzoate*). There is evidently a double decomposition between two molecules:

$$\left\{ \begin{matrix} C_2 & H_3 & O \\ C_7 & H_5 & O \end{matrix} \right\} O + \left\{ \begin{matrix} C_2 & H_3 & O \\ C_7 & H_5 & O \end{matrix} \right\} O = \left\{ \begin{matrix} C_2 & H_3 & O \\ C_2 & H_3 & O \end{matrix} \right\} O + \left\{ \begin{matrix} C_7 & H_5 & O \\ C_7 & H_5 & O \end{matrix} \right\} O$$
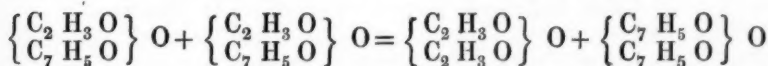
This reaction perfectly explains the formation of anhydrous acetic acid, as described in my last communication (from benzoic chloride and acetate of potassium).

Acetic cuminate or *cuminic acetate*, is obtained in the same manner as the above anhydride. Freshly prepared, it is a fragrant oil, which preserves its liquid form in a stoppered bottle; but a few moments contact with the air is sufficient to make it crystallise, magnificent needles being formed, until the mass assumes the appearance and consistency of frozen olive oil. Analysis shews that this change of state is accompanied by no change of composition of the body:

$$C_{12} H_{14} O_3 = \left\{ \begin{matrix} C_2 & H_3 & O \\ C_{10} & H_{11} & O \end{matrix} \right\} O$$
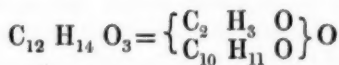
I have also succeeded in preparing in a state of purity, *benzoic cinnamate*, or *cinnamic benzoate*, a heavy, almost inodorous oil, containing·

$$C_{16} H_{12} O_3 = \begin{Bmatrix} C_7 & H_5 & O \\ C_9 & H_7 & O \end{Bmatrix} O;$$
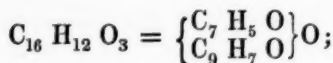
as well as the *benzoic cuminate* or *cuminic benzoate*, a similar heavy oil, containing :

$$C_{17} H_{16} O_3 = \begin{Bmatrix} C_7 & H_5 & O \\ C_{10} & H_{11} & O \end{Bmatrix} O$$
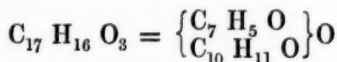
Finally also, *anhydrous cuminic acid*, or *cuminic cuminate*, is obtained by the same process, in the form of a heavy oil, resembling a fatty oil, and possessing a very faint smell. This oil also crystallises after a time ; but the oil and the crystals present the same

composition, $C_{20} H_{22} O_3 = \begin{Bmatrix} C_{10} & H_{11} & O \\ C_{16} & H_{11} & O \end{Bmatrix} O$
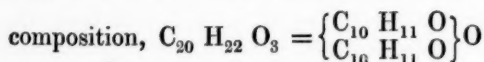
I am continuing these experiments with butyric, valerianic, and nitrobenzoic acids, and hope soon to be able to communicate my results to the Society.

In concluding this notice, I wish to call the attention of chemists to a remarkable analogy which exists between certain organic compounds belonging to the type water, and certain others, which I compare to the type hydrogen, as represented by the following parallel, which I submit to the consideration of experimenters.

$\begin{matrix} H \\ H \end{matrix}$ } Free hydrogen	$\begin{matrix} H \\ H \end{matrix}$ } O Water	
$\begin{matrix} C_2 H_5 \\ H \end{matrix}$ } Hydride of Ethyl, homologous to marsh-gas	$\begin{matrix} C_2 H_5 \\ H \end{matrix}$ } O Alcohol.	
$\begin{matrix} C_2 H_5 \\ C_2 H_5 \end{matrix}$ } Ethyl	$\begin{matrix} C_2 H_5 \\ C_2 H_5 \end{matrix}$ } O Ether.	
$\begin{matrix} C_2 H_3 O \\ H \end{matrix}$ } Aldehyde	$\begin{matrix} C_2 H_3 O \\ H \end{matrix}$ } O Acetic acid.	
$\begin{matrix} C_2 H_3 O \\ C_2 H_3 O \end{matrix}$ } Acetyl, to be found	$\begin{matrix} C_2 H_3 O \\ C_2 H_3 O \end{matrix}$ } O Anhydrous acetic acid.	
$\begin{matrix} C_2 H_3 O \\ C H_3 \end{matrix}$ } Acetone	$\begin{matrix} C_2 H_3 O \\ C H_3 \end{matrix}$ } O Acetate of Methyl.	

This comparison enables me to foretel that acetyl, and in general those oxygenised groups which act like hydrogen (oxygenised radicals), will be obtained by the reaction of the corresponding chlorides on the metallic aldehydes ; and in like manner the ketones, by acting on the metallic aldehydes by the hydrochloric ethers. The experiments and considerations published on this last point by M. Chancel seem to me quite decisive.

NOTICES

OF

Papers contained in other Journals.

Report upon "Original Gravities,"
By Professors Graham, Hofmann, and Redwood.

ADDRESSED TO THE CHAIRMAN OF THE BOARD OF INLAND REVENUE.

SIR,

The subject of the present inquiry is the specific gravity of the worts of beer. When worts are fermented they lose in density, and assume, as beer, a different specific gravity. This last is of course the only true specific gravity of the beer, but the specific gravity of the worts is also named with reference to the beer, as the original specific gravity of the beer, or the original gravity of the beer.

A knowledge of the original gravity of beer is required to fix the drawback allowed upon beer when exported, according to the terms of 10th Victoria, cap. 5. By this Act a drawback is granted of five shillings per barrel of thirty-six gallons, upon beer exported, of which " the worts used before fermentation were of not less specific gravity than 1·054, and not greater specific gravity than 1·081 ;" and a drawback of seven shillings and sixpence per barrel upon beer, of which " the worts used before fermentation were not of less specific gravity than 1·081."

The original gravity of beer is directly observed by the brewer only, who ascertains the specific gravity of the worts of each brewing operation by means of the saccharometer, or other form of the hydrometer, and preserves a record of the observation. To enable the revenue officer to arrive independently at the same information, he possesses the beer only from which to infer the specific gravity of the worts. It is the special object of the following investigations to discover how the original gravity of beer may be ascertained most accurately from the properties of the beer itself.

The question has already been examined by foreign chemists—by Otto and Zenneck, and especially by Balling of Prague; as well as by Messrs. Dobson and Phillips of the department of Inland

Revenue, whose previous researches have greatly facilitated the present inquiry.

The same properties of the beer have been generally had recourse to as likely to throw light upon the original gravity of the liquid, and obviously suggest themselves. These are—1°, the specific gravity of the beer itself (the beer gravity); 2°, the proportion of alcohol the beer contains (the spirit-indication of the beer), to be ascertained by distillation and other practical methods; and 3°, the proportion of unfermented solid matter held in solution by the beer (the extract or extractive matter of the beer). The liquid from which the volatile alcohol has been expelled, and which contains the extractive matter, when made up again to the original volume of the beer by the addition of the necessary quantity of water, represents the beer without its spirit; and it is by the greater or less specific gravity of this liquid that the proportion of extract in the beer has been generally estimated. The extract gravity of the beer is thus obtained.

As the alcohol of the beer is derived from the decomposition of saccharine matter only, and represents approximately double its weight of starch-sugar, a speculative original gravity might be obtained by simply increasing the extract gravity of the beer by that of the quantity of starch-sugar known to be decomposed in the fermentation. The inquiry would then reduce itself to the best means of ascertaining the two experimental data, namely, the extract gravity and the proportion of alcohol in the beer, particularly of the latter. It would be required to decide whether the alcohol should be determined from the gravity of the spirits distilled from the beer; by the increased gravity of the beer when its alcohol is evaporated off; by the boiling point of the beer, which is lower the larger the proportion of alcohol present; or by the refracting power of the beer upon light—various methods recommended for the valuation of the spirits in beer.

Original gravities so deduced, however, are found to be useless, being in error and always under the truth, to an extent which has not hitherto been at all accounted for. The theory of brewing, upon a close examination of the process, proves to be less simple than is implied in the preceding assumption; and other changes appear to occur in worts, simultaneously with the formation of alcohol, which would require to be allowed for before original gravities could be rightly estimated. It was found necessary to study the gravity in solution of each by itself, of the principal chemical substances which are found in fermented liquids. These individual gravities defined the possible range of variation in original gravity, and they brought out clearly for the first time the nature of the agencies which chiefly affect the result.

The use of cane-sugar is now permitted in breweries, and the solution of sugar may be studied first as the wort of simplest composition. The tables of the specific gravity of sugar solutions, con-

structed by Mr. Bate, have been verified, and are considered entirely trustworthy. The numbers in the first and third columns of Table I., which follows, are, however, from new observations. It is to be remarked that these numbers have all reference to weights, and not to measures. A solution of cane-sugar, which contains 25 grains of sugar in 1000 grains of the fluid, has a specific gravity of 1010·1, referred to the gravity of pure water taken as 1000 ; a solution of 50 grains of cane sugar in 1000 grains of the fluid, a specific gravity of 1020·2, and so on. The proportion of carbon contained in the sugar is expressed in the second column ; the numbers being obtained from the calculation that 171 parts by weight of cane-sugar ($C_{12} H_{11} O_{11}$) consist of 72 parts of carbon, 11 parts of hydrogen, and 88 parts of oxygen ; or of 72 parts of carbon combined with 99 parts of the elements of water. It is useful to keep thus in view the proportion of carbon in sugar solutions, as that element is not involved in several of the changes which precede or accompany the principal change which sugar undergoes during fermentation, and which changes only affect the proportion of the oxygen and hydrogen, or elements of water, combined with the carbon. The proportion of oxygen and hydrogen in the altered sugar increases or diminishes during the changes referred to ; but the carbon remains constant, and affords, therefore, a fixed term in the comparison of different solutions.

TABLE I.

SPECIFIC GRAVITY OF SOLUTIONS OF CANE-SUGAR IN WATER.

Cane-Sugar, in 1000 parts by weight.	Carbon in 1000 parts by weight.	Specific Gravity.
25	10·53	1010·1
50	21·05	1020·2
75	31·58	1030·2
100	42·10	1040·6
125	52·63	1051
150	63·16	1061·8
175	73·68	1072·9
200	84·21	1083·8
225	94·73	1095·2
250	105·26	1106·7

When yeast is added to the solution of cane-sugar in water, or to any other saccharine solution, and fermentation commenced, the specific gravity is observed to fall, owing to the escape of carbonic acid gas, and the formation of alcohol, which is specifically lighter than water ; 171 grains of sugar, together with 9 grains of water, being converted into 92 grains of alcohol and 88 grains of carbonic acid ($C_{12} H_{11} O_{11} + HO = 2 C_4 H_6 O_2 + 4 CO_2$). But if the process of fer-

mentation be closely watched, the fall of gravity in cane-sugar will be found to be preceded by a decided increase of gravity. Solutions were observed to rise from 1055 to 1058, or 3 degrees of gravity, within an hour after the addition of the yeast, the last being in the usual proportion for fermentation. When the yeast was mixed in minute quantity only, such as $\frac{1}{300}$ of the weight of the sugar, the gravity of the sugar solution rose gradually in four days from 1055 to 1057·91, or also nearly 3 degrees; with no appearance, at the same time, of fermentation or of any other change in the solution. This remarkable increase of density is owing to an alteration which takes place in the constitution of the cane-sugar, which combines with the elements of water and becomes starch-sugar, a change which had been already proved by H. Rose and by Dubrunfaut, to precede the vinous fermentation of cane-sugar. The same conversion of cane-sugar into starch-sugar, with increase of specific gravity, may be shown by means of acids as well as of yeast. A solution of 1000 parts of cane-sugar in water, having the specific gravity 1054·64, became with 1 part of crystallised oxalic acid added to it 1054·7; and being afterwards heated for twenty-three hours to a temperature not exceeding 128° Fahr., it was found (when cooled) to have attained a gravity of 1057·63—an increase again of nearly 3 degrees of gravity.

In the table of starch-sugar, which follows, the influence of this conversion upon specific gravity is shown by placing together the gravities of cane-sugar and of the starch-sugar into which it is convertible, and which therefore contain equal quantities of carbon.

TABLE II.

COMPARISON OF THE SPECIFIC GRAVITIES OF SOLUTIONS OF CANE-SUGAR AND STARCH-SUGAR CONTAINING EQUAL QUANTITIES OF CARBON.

Cane-Sugar contained in 1000 parts by weight of Solution.	Specific gravity of solution of Cane-Sugar.	Specific gravity of solution of Starch-Sugar.
25	1010·1	1010·4
50	1020·2	1020·8
75	1030·2	1031·3
100	1040·6	1042·4
125	1051	1053·5
150	1061·8	1064·9
175	1072·9	1076
200	1083·8	1087·8
225	1095·2	1099·4
250	1106·7	1111·4

When yeast is added to a solution of starch-sugar, or of cane-sugar previously converted by means of oxalic acid, or by yeast itself, into starch-sugar, the rise of gravity described is no longer observed to precede fermentation.   Hence the irregularity does not appear in an infusion of malt, which contains starch-sugar, and the attenuation of malt worts commences with the first action of the yeast, and advances without interruption till the fermentation is completed.

It is already evident from these statements, that the original gravity of a fermented liquid or beer must be different, according as it was derived from a wort of cane-sugar or of starch-sugar.

A comparison was next made of the specific gravities of solutions of pale and of brown malt with the solutions of the two pure sugars. The carbon determined by actual combustion in organic analysis, is the same in all the four solutions, of which the gravities are given in the same line, and is the proportion which exists in 25, 50, 75, &c., parts of cane-sugar, as in Table I.

TABLE III.

SPECIFIC GRAVITY OF SOLUTIONS OF PALE MALT, BROWN MALT, AND STARCH-SUGAR, CONTAINING EQUAL QUANTITIES OF CARBON.

Solution of Pale Malt.	Solution of Brown Malt.	Solution of Starch-Sugar.	Parts of Cane-Sugar corresponding in 1000 parts by weight of Solution.
1010·0	1010·0	1010·4	25
1020·3	1020·2	1020·8	50
1030·6	1030·6	1031·3	75
1041·2	1041·2	1042·4	100
1052·1	1052·0	1053·5	125
1063·0	1062·9	1064·9	150
1074·2	1074·0	1076·0	175
1085·5	1085·5	1087·8	200
1097·2	1097·2	1099·4	225
1109·0	1109·0	1111·4	250

It is interesting to observe how closely the gravities of the pale and brown malt agree together through the whole range of the Table. The gravities are often identical, and in no case differ more than 0·2 degree.   This indicates a greater uniformity of density in the worts of different varieties of malt than could have been anticipated, and it gives a character of constancy to the density of malt wort, which is highly satisfactory.

The density of the malt worts also approaches that of the pure starch-sugar, but is always a little less by about 1 degree of gravity

in 35. Malt wort appears, indeed, intermediate between the two pure sugars. We have, for instance, solutions containing an equal quantity of carbon, which exhibit the following gravities:

Cane-Sugar	.	.	.	1072·9
Pale Malt .	.	.	.	1074·2
Starch-Sugar	.	.	.	1076·0

Now, if the whole carbon of malt wort were present in the form of starch-sugar, the gravity of the wort should somewhat exceed that of the pure starch-sugar solution, as a small proportion of alkaline and earthy salts exist in the malt infusion, and must add to its gravity. The carbon present in the small quantity of albumen of the malt could not affect the result materially in either way.

But there are two other substances related to sugar, of which the interference in malt infusions may be anticipated, namely, Dextrin, or the gum of starch, and Caramel. These are both forms of the sugar principle, the transition from the one condition to the other depending upon the fixation of the elements of water in the substance, or the liberation of a proportion of water. Observations were in consequence made of the gravities of pure solutions of dextrin prepared from starch, and of caramel produced by the proper application of heat to sugar.

TABLE IV.

SPECIFIC GRAVITIES OF SOLUTIONS OF CARAMEL, DEXTRIN, AND STARCH-SUGAR, CONTAINING EQUAL QUANTITIES OF CARBON.

Solution of Caramel.	Solution of Dextrin.	Solution of Starch-Sugar.	Parts of Cane-Sugar corresponding in 1000 parts by weight of Solution.
1008·7	1009·7	1010·4	25
1017·3	1019·3	1020·8	50
1026·2	1028·8	1031·3	75
1034·9	1038·3	1042·4	100
1043·8	1047·9	1053·5	125
1052·8	1057·3	1064·9	150
1062·3	1066·9	1076·0	175
1071·8	1067·6	1087·8	200
1081·3	1086·3	1099·4	225
1091·0	1095·8	1111·4	250

It will be observed that the gravities of both caramel and dextrin are considerably less than those of starch-sugar, and that consequently

the presence of either of these substances, taking the place of starch-sugar in a malt infusion, must lower the specific gravity of the latter. The following solutions of the three different substances, containing the same quantity of carbon, appear by the Table to have different gravities:

Starch-Sugar	.	.	.	1076
Dextrin	.	.	.	1066·9
Caramel	.	.	.	1062·3

The solution of cane-sugar containing the same quantity of carbon, has the specific gravity of 1072·9, and contains 175 grains of cane-sugar in 1000 grains of the solution, or 17·5 per cent of cane-sugar. It follows that this proportion of the saccharine principle may present itself with specific gravities varying from 1076 to 1062·3, in the different forms which it can assume. A certain quantity of dextrin generally exists in the wort of malt, which may be thrown down by alcohol. Dextrin was prepared in a pure state from this source. Its presence is, of course, due to the incomplete saccharization of the starch of malt in the process of mashing.

With regard to the existence of the other substance, caramel, in malt infusions, the extreme facility with which starch-sugar is altered by heat, would lead us to look for the production of caramel in the kiln-drying of malt, particularly of brown malt. Its production is indicated by the dark colour of the infusion of the highly dried malt. Of the 3 or 4 per cent of black malt used for colouring porter, the whole soluble portion appears also to be caramel. It may be further added, that the use of caramel prepared from sugar, as a colouring ingredient of porter, is now permitted in breweries.

A substance resembling caramel in some of its properties is developed in fermented liquids in another way. The saccharine matter of the wort is never wholly converted into carbonic acid and alcohol in the most favourable circumstances, a portion of solid matter always remaining, which is no further fermentable even after the alcohol is distilled off and fresh yeast applied. This residuary matter is generally spoken of as a gummy substance, but when obtained by the fermentation of pure sugar, it partakes more of the characters of caramel, or of glucic acid, particularly in the low gravity of its solution in water. Of pure cane-sugar fermented, 4·4, 3·72, and 3·7 per cent was converted into this substance in three fermentations, in which one and a half, three, and six measures of yeast were employed to one hundred measures of solution, containing one-seventh of its weight of sugar.

The extractive substance resembling caramel was obtained in the form of a dark brown syrup, by evaporating the liquid after fer-

mentation had entirely ceased.   It reddened litmus-paper, contained
lactic acid, and was distinctly sour and slightly bitter to the taste.
That this residuary substance contained no longer any starch-sugar,
appeared from the fact, that on mixing its diluted solution with
caustic potash, and heating it, the colour was not sensibly darkened.
It was no longer fermentable by yeast, and it did not become so (like
dextrin) after being boiled with sulphuric acid. It resembled caramel
in giving with sulphate of copper and caustic potash in excess a
transparent blue solution, from which suboxide of copper was thrown
down on the application of heat.   It is precipitated by baryta-water,
and gives with subacetate of lead a brown precipitate, which, how-
ever, is more voluminous and paler in colour than the precipitate
from pure caramel. Neutral acetate of lead precipitates a portion
only of this substance, proving that it is not a single principle, but a
mixture of two or more substances.

A solution of it compared with that of caramel, obtained by heating
cane-sugar to 410° Fahr., and both containing the same proportions
of carbon, gave very similar densities.

TABLE V.

SPECIFIC GRAVITIES OF SOLUTIONS OF CARAMEL FROM CANE-SUGAR, AND OF
THE EXTRACTIVE SUBSTANCE FROM THE FERMENTATION OF SUGAR, CONTAINING
EQUAL QUANTITIES OF CARBON.

Solution of Caramel.	Solution of Extractive Substance.	Parts of Cane-Sugar corresponding, in 1000 parts by weight of Solution.
1008·7	1008·9	25
1017·3	1017·8	50
1026·2	1026·5	75
1034·9	1035·5	100
1043·8	1044·7	125
1052·8	1053·9	150
1062·3	1063·0	175
1071·8	1072·7	200
1081·3	1082·3	225

This extractive substance appears to interfere more than dextrin in
giving lightness or apparent attenuation to fermented worts, without
a corresponding production of alcohol. Its effect becomes the more
sensible the more nearly the worts are exhausted by fermentation. It
is produced in the fermentation of both kinds of sugar and also of
malt. There appears to be a certain uniformity in the proportion of
saccharine matter which undergoes this change in every brewing,

judging from the correspondence of different beers in their gravities, at the same stage of fermentation, which shall afterwards be exhibited. It causes a marked irregularity in the progression of the gravities when the fermentation is carried to an extreme, as it is in distilleries; but in brewing beer the fermentation is always arrested at a point in its progress too early to allow the effect of the extractive substance upon the gravity to become very conspicuous.

The indication by gravity of the extractive substance is so much lower than that of starch-sugar, that the former substance only indicates about five-sixths of the saccharine principle which has given rise to it. Hence it is that original gravities cannot be calculated on the assumption that the solid matter in beer is sugar, or a substance having the same gravity as sugar.

In the maturation of beer by time, an increase of attenuation is observed, which is no doubt chiefly due to the slow continuation of the vinous fermentation, with the disappearance of sugar and formation of alcohol; but there is some reason to believe that the attenuation is not entirely due to that cause. Part of the loss of gravity appears to be occasioned by the change in condition of the saccharine principle from that of starch-sugar to the condition of the extractive substance, a change which involves a loss of specific gravity without a corresponding production of alcohol.

Another constituent of malt wort, which should not be omitted, is the soluble azotized or albuminous principle derived from the grain. The nitrogen was determined in a strong wort of pale malt with hops, of the specific gravity 1088, and containing about 21 per cent of solid matter. It amounted to 0·217 per cent. of the wort, and may be considered as representing 3·43 per cent of albumen. In the same wort, after being fully fermented, the nitrogen was found to amount to 0·134 per cent, equivalent to 2·11 per cent of albumen. The loss observed of nitrogen and albumen may be considered as principally due to the production and growth of yeast, which is an insoluble matter, at the cost of the soluble albuminous matter. Solutions of egg-albumen in water, containing 3·43 and 2·11 per cent respectively of that substance, were found to have the specific gravities of 1004·2 and 1003·1. Hence a loss of density has occurred during fermentation of 1·1 degree on a wort of 1088 original gravity, which can be referred to a change in the proportion of albuminous matter. It will be observed that the possible influence of this substance and of the greater or less production of yeast during fermentation, upon the gravity of beer, are restricted within narrow limits.

The mineral constituents of the same worts, consisting of soluble salts of the earths and alkalies, amounted before fermentation to 0·443 per cent, and after fermentation to 0·463 per cent. The

proportion of these substances may therefore be supposed to remain constant.

The process required for the determination of the original gravity of beer, must be easy of execution, and occupy little time. It is not proposed, in the examination of a sample, to separate by chemical analysis the several constituents which have been enumerated. In fact, we are practically limited to two experimental observations on the beer, in addition to the determination of its specific gravity.

One of these is the observation of the amount of solid or extractive matter still remaining after fermentation, which is always more considerable in beer than in the completely fermented wash of spirits. A known measure of the beer might be evaporated to dryness, and the solid residue weighed, but this would be a troublesome operation, and could not indeed be executed with great accuracy. The same object may be attained with even a more serviceable expression for the result, by measuring exactly a certain quantity of the beer, such as four fluid ounces, and boiling it down to somewhat less than half its bulk in an open vessel, such as a glass flask, so as to drive off the whole alcohol. The liquid when cool is made up to four fluid ounces, or the original measure of the beer, and the specific gravity of this liquid is observed. It has already been referred to as to the extract gravity of the beer, and represents a portion of the original gravity. Of a beer of which the history was known, the original gravity of the malt wort was 1121, or 121 degrees; the specific gravity of the beer itself before evaporation, 1043; and the extract gravity of the beer 1056·7, or 56·7 degrees.

The second observation which can be made with sufficient facility upon the beer, is the determination of the quantity of alcohol contained in it. This information may be obtained most directly by submitting a known measure of the beer to distillation, continuing the ebullition till all the alcohol is brought over, and taking care to condense the latter without loss. It is found in practice that four ounce-measures of the beer form a convenient quantity for the purpose. This quantity is accurately measured in a small glass flask, holding 1750 grains of water when filled up to a mark in the neck. The mouth of the small retort containing the beer is adapted to one end of a glass tube-condenser, the other end being bent and drawn out for the purpose of delivering the condensed liquid into the small flask previously used for measuring the beer. The spirituous distillate should then be made up with pure water to the original bulk of the beer, and the specific gravity of the last liquid be observed by the weighing bottle, or by a delicate hydrometer, at the temperature of 60° Fahr. The lower the gravity the larger will be the proportion of alcohol, the exact amount of which may be learned by reference to the proper tables of the gravity of spirits. The spirit-gravity of the

beer already referred to, proved to be 985·95 ; or it was 14·05 degrees of gravity less than 1000 or water. The "spirit-indication" of the beer was therefore 14·05 degrees; and the extract gravity of the same beer 56·7 degrees.

The spirit-indication and extract gravity of any beer being given, do we possess data sufficient to enable us to determine with certainty the original gravity ? It has already been made evident that these data do not supply all the factors necessary for reaching the required number by calculation.

The formation of the extractive matter, which chiefly disturbs the original gravity, increases with the progress of the fermentation ; that is, with the proportion of alcohol in the fermenting liquor. But we cannot predicate from theory any relation which the formation of one of these substances should bear to the formation of the other, and are unable, therefore, to say beforehand that because so much sugar has been converted into alcohol in the fermentation, therefore so much sugar has also been converted into the extractive substance. That a uniform, or nearly uniform relation, however, is preserved in the formation of the spirits and extractive substance, in beer-brewing, appears to be established by the observations which follow. Such an uniformity in the results of the vinous fermentation is an essential condition for the success of any method whatever of determining original gravities, at least within the range of circumstances which affect beer-brewing. Otherwise two fermented liquids of this class, which agree in giving both the same spirit-indication and the same extractive gravity, may have had different original gravities, and the solution of our problem becomes impossible.

The fermentation of liquids of known composition and original gravity, containing pure cane-sugar, pure starch-sugar, and the soluble matter of malt, the latter both with and without hops, was now repeated, and the wort examined in each fermentation at ten or twelve different stages of its progress, or after short periods of a few hours. The two required observations of the spirit-indication and extract gravity were made on every occasion, with certain additional observations which shall again be referred to.

The details of these and the numerous other fermentations referred to, were conducted, under our directions, by Mr. Adam Young and Mr. C. B. Forsey (officers of Inland Revenue), lately of the Birkbeck Laboratory, to whom we have great pleasure in acknowledging our obligations for the valuable aid which a perfect acquaintance with the subject, and remarkable skill in experimenting, combined with the most untiring zeal, could supply.

The results of a particular fermentation of cane-sugar may be stated. Fifteen and a half pounds of refined sugar were dissolved in 10 gallons of water, making $10\frac{7}{8}$ gallons of solution, of which the

specific gravity was 1055·3 at 60°; and after adding three fluid pounds of fresh porter yeast, the specific gravity was 1055·95. The original gravity may be taken as 1055·3 (55·3 degrees).

FERMENTATION OF SUGAR-WORT OF ORIGINAL GRAVITY 1055·3.

I. Number of Observation.	II. Period of Fermentation.		III. Degrees of Spirit Indication.	IV. Degrees of Extract Gravity.	V. D egree of Extract Gravity *lost*.
	Days.	Hours.			
1	0	0	0	55·30	0·
2	0	6	1·59	52·12	3·18
3	0	12	2·57	47·82	7·48
4	0	19	3·60	43·62	11·68
5	0	23	4·33	40·13	15·17
6	1	5	5·31	35·50	19·80
7	1	12	6·26	31·39	23·91
8	1	19	7·12	27·63	27·67
9	2	11	8·59	20·26	35·04
10	3	11	9·87	13·40	41·90
11	5	12	10·97	7·60	47·70
12	6	12	11·27	4·15	51·15

Columns III. and V. respectively exhibit the spirit which has been produced, and the solid matter which has disappeared; the first in the form of the gravity of the spirit, expressed by the number of degrees it is lighter than water, or under 1000, and the second by the fall in gravity of the solution of the solid matter remaining below the original gravity 1055·3. This last value will be spoken of as "degrees of gravity lost;" it is always obtained by subtracting the extract gravity (column IV.) from the known original gravity. To discover whether the progress of fermentation has the regularity ascribed to it, it was necessary to observe whether the same relation always holds between the columns of "degrees of spirit-indication" and "degrees of gravity lost." It was useful, with this view, to find what degrees lost corresponded to whole numbers of degrees of spirit-indication. This can be done safely from the preceding Table, by interpolation, where the numbers observed follow each other so closely. The corresponding degrees of spirit-indication and of gravity lost, as they appear in this experiment upon the fermentation of sugar, are as follows:

FERMENTATION OF SUGAR-WORT, OF ORIGINAL GRAVITY 1055·3.

Degrees of Spirit-Indication.	Degrees of Extract Gravity lost.
1	1·71
2	4·74
3	9·26
4	13·48
5	18·30
6	22·54
7	27·01
8	31·87
9	37·12
10	42·55
11	47·88

In two other fermentations of cane-sugar, the degrees of gravity lost, found to correspond to the degrees of spirit-indication, never differed from the numbers of the preceding experiment, or from one another, more than 0·9 degree of gravity lost. This is a sufficiently close approximation.

FERMENTATION OF SUGAR-WORT OF ORIGINAL GRAVITY 1054·7, A; AND OF SUGAR-WORT OF ORIGINAL GRAVITY 1028·8, B.

Degrees of Spirit-Indication.	Degrees of Extract Gravity lost.	
	A.	B.
1	2·01	1·94
2	5·15	4·84
3	9·22	9·90
4	13·95	14·10
5	18·09	18·31
6	23·16	22·61
7	27·05	27·51
8	32·26	
9	37·40	
10	42·16	
11	47.56	

The observations of the three experiments were combined in the following Table, which exhibits the mean results. Besides the degrees

of gravity lost corresponding to whole degrees of spirit-indication, the degrees of gravity lost corresponding to tenths of a degree of spirit-indication are added from calculation.

TABLE VI.—CANE-SUGAR:

DEGREES OF SPIRIT-INDICATION WITH CORRESPONDING DEGREES OF GRAVITY LOST.

Degrees of Spirit-Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·2	·3	·5	·7	·9	1·0	1·2	1·4	1·6
1	1·9	2·1	2·4	2·7	3·0	3·3	3·6	3·9	4·2	4·6
2	5·0	5·4	5·8	6·2	6·6	7·0	7·5	8·0	8·5	9·0
3	9·5	9·9	10·3	10·7	11·2	11·6	12·0	12·4	12·8	13·3
4	13·8	14·2	14·6	15·0	15·5	15·9	16·3	16·7	17·2	17·7
5	18·3	18·7	19·1	19·5	19 9	20·3	20·8	21·2	21·7	22·2
6	22·7	23·1	23·5	23·9	24·4	24·7	25·2	25·6	26·1	26·6
7	27·1	27·6	28·1	28·6	29·1	29·6	30·0	30·5	31·0	31·5
8	32·0	32·5	33·0	33·5	34·0	34·5	35·0	35·5	36·0	36·6
9	37·2	37·7	38·2	38·7	39·2	39 7	40·3	40·8	41·3	41·8
10	42·4	42·9	43·4	44·0	44·5	45·0	45·6	46·1	46·6	47·2
11	47·7									

It is seen from this Table that for 5 degrees of spirit-indication, the corresponding degrees of gravity lost are 18·3 degrees. For 5·9 degrees of spirit-indication, the corresponding degrees of gravity lost are 22·2 degrees.

This Table is capable of a valuable application, for the sake of which it was constructed. By means of it, the unknown original gravity of a fermented liquid, or beer, from cane-sugar, may be discovered, provided the spirit-indication and extract gravity of the beer are observed. Opposite to the spirit-indication of the beer in the Table, we find the corresponding degrees of gravity lost, which last, added to the extract gravity of the beer, gives its original gravity.

Suppose the sugar-beer exhibited an extract gravity of 7·9 degrees (1007·9), and spirit-indication of 11 degrees. The latter marks, according to the Table, 47·7 degrees of gravity lost, which added to the observed extract gravity, 7·9 degrees, gives 55·6 degrees of original gravity for the beer (1055·6).

The table which follows was constructed in the same manner for starch-sugar, from two fermentations of the pure substance, and gives the means of calculating the original gravity of liquids fermented from starch-sugar, when the spirit-indication and extract gravity of the beer are known from experiment. The extreme deviation between the two series of observations was 0·8 degree of gravity lost.

TABLE VII.—STARCH-SUGAR.

DEGREES OF SPIRIT-INDICATION WITH CORRESPONDING DEGREES OF GRAVITY LOST.

Degrees of Spirit-Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	.9
0	—	·3	·6	·9	1·2	1 5	1·8	2·1	2·4	2·7
1	3·0	3·3	3·7	4·0	4·4	5·0	5·0	5·4	5·8	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·3
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·7	14·1	14·5
4	15·0	15·4	15·9	16·4	16·8	17·3	17·7	18·2	18·7	19·2
5	19·7	20·1	20·6	21·0	21·5	22·0	22·5	23·0	23·5	24·0
6	24·5	25·0	25·4	25·9	26·4	26·8	27·3	27·8	28·3	28·8
7	29·3	29 7	30·2	30·7	31·1	31·6	32·0	32·5	33·0	33·5
8	34·0	34·5	35·0	35·5	36·0	36·5	37·0	37·5	38·0	38·5
9	39·0	39·5	40·1	40·6	41·1	41·7	42·2	42·8	43·3	43·9
10	44·5	45·1	45·8	46·5						

The numbers will be observed to differ from those of the preceding Table for cane-sugar, and to be all greater, the differences increasing pretty uniformly with the higher degrees of spirit-indication. The corresponding numbers for 10 degrees of spirit-indication are 42 4 in cane-sugar, and 44·5 in starch-sugar, or a difference of 2·1 degrees of gravity lost. By this difference the original gravity of the beer of starch-sugar is increased over that of cane-sugar, as should be the case; the specific gravity of starch-sugar being always higher than that of cane-sugar containing an equal weight of carbon, and capable of yielding an equal quantity of spirits. (See Table II.)

The three Tables for malt worts of different kinds which follow, will be found to agree well with each other, and also to accord closely with the preceding Table for pure starch-sugar worts.

TABLE VIII.—PALE MALT WITHOUT HOPS.

DEGREES OF SPIRIT-INDICATION WITH CORRESPONDING DEGREES OF GRAVITY LOST.

Degrees of Spirit-Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·3	·6	·9	1·2	1·5	1·8	2·2	2·5	2·8
1	3·2	3·6	3 9	4·3	4·6	5·0	5·4	5·8	6·2	6·6
2	7·0	7·4	7·8	8 2	8·6	8·9	9·4	9·8	10·3	10·7
3	11·2	11·6	12·1	12·6	13 0	13·4	13·8	14·2	14·6	15·0
4	15·5	15·9	16·4	16·9	17·3	17·7	18·1	18·6	19·1	19·5
5	20·0	20·5	20·9	21·3	21·8	22·2	22·7	23·1	23·6	24·1
6	24·6	25·0	25·5	25·9	26·3	26·8	27·3	27·8	28·3	28·8
7	29·3	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2	33·7
8	34·2	34·7	35·2	35·7	36·3	36·9	37·5	38·1	38·6	39 1
9	39·5	40·0	40·5	41·0						

The results given are the means of the observations of two fermentations of pale malt without hops, which accorded throughout within 1 degree of gravity.

TABLE IX.—PALE MALT WITH HOPS.

DEGREES OF SPIRIT-INDICATION WITH CORRESPONDING DEGREES OF GRAVITY LOST.

Degrees of Spirit-Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·2	·5	·7	1·0	1·3	1·6	1·9	2·2	2·5
1	2·8	3·1	3·4	3·7	4·0	4·4	4·8	5·2	5·5	5·9
2	6·3	6·7	7·1	7·5	8·0	8·4	8·8	9·2	9·6	10·0
3	10·5	10·9	11·3	11·8	12·2	12·7	13·1	13·6	14·0	14·5
4	15·0	15·4	15·8	16·3	16·7	17·1	17·6	18·0	18·5	19·0
5	19·5	19·9	20·4	20·9	21·3	21·7	22·2	22·7	23·1	23·5
6	23·9	24·4	24·8	25·3	25·7	26 2	26·6	27·0	27·4	27·9
7	28·4	28·9	29·4	29·9	30·4	30·8	31·2	31·7	32·2	32·7
8	33·2									

The results are the means of the observations of two fermentations of pale malt with hops, which corresponded throughout within 0·49 degree of gravity lost.

TABLE X.—BROWN AND PALT MALT.—EQUAL WEIGHTS.

DEGREES OF SPIRIT-INDICATION WITH CORRESPONDING DEGREES OF GRAVITY LOST.

Degrees of Spirit-Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·3	·6	·9	1·2	1·5	1·8	2·1	2·4	2·8
1	3·1	3·4	3·7	4·0	4·3	4·7	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·5	10·8	11·3	11·7	12·2	12·6	13·0	13·5	13·9	14·0
4	14·8	15·2	15·6	16·1	16·5	17·0	17·4	17·8	18·2	18·6
5	19·0	19·4	19·8	20·2	20·6	21·0	21·5	22·0	22·5	23·0
6	23·5	23·9	24·4	24·9	25·4	25·9	26·4	26·9	27·4	27·9
7	28·2	28·7	29·2	29·8	30·3	30·8	31·3	31·9	32·4	32·9
8	33·5	34·2	34·9	35·8						

This table was derived from a single experiment. No observation could be made upon brown malt alone, as it could not be fully fermented without a considerable admixture of pale malt.

For comparison, the numbers corresponding to the integral degrees of spirit-indication of the five different Tables are placed together in the following Table:

TABLE XI.—VARIOUS WORTS.

DEGREES OF SPIRIT-INDICATION WITH CORRESPONDING DEGREES OF GRAVITY LOST.

Degrees of Spirit-Indication.	I. Cane-Sugar.	II. Starch-Sugar.	III. Pale Malt.	IV. Pale Malt with Hops.	V. Brown and Pale Malt.	VI. Mean of ii, iii, iv, & v.
1	1·9	3·0	3·2	2·8	3·1	3·0
2	5·0	6·6	7·0	6·3	6·6	6·6
3	9·5	10·7	11·2	10·5	10·5	10·7
4	13·8	15·0	15·5	15·0	14·8	15·1
5	18·3	19·7	20·0	19·5	19·0	19·5
6	22·7	24·5	24·6	23·9	23·5	24·1
7	27·1	29·3	29 3	28·4	28·2	28·8
8	32·0	34·0	34·2	33·2	33 5	33·9
9	37·2	39·0	39 5	—	—	39·25
10	42·4	44·5	—	—	—	44·5
11	47·7					

The first point which excites attention is the general similarity of all the four columns which refer to liquids containing the same fermentable substance, starch-sugar. In comparing together columns II. and III., those of starch-sugar itself and pale malt without hops, the greatest difference observed between any two corresponding numbers is 0·5, or half a degree of gravity. The numbers of the two columns are the same at one point, but at all other places the starch-sugar column is slightly exceeded by the pale malt column. It thus appears that the phenomena of the fermentation of pale malt are closely represented by a solution of pure starch-sugar. The other substances besides sugar, of which small quantities are known to be present in malt, appear therefore not to be subjected to any change during the fermentation of the wort, which materially affects the gravity of the latter. The addition of hops to the malt has a slight effect in lowering the gravity numbers, as seen in column IV., to the extent at one point of 1 degree of gravity. Brown malt appears to act in the same direction as hops upon the progression of gravities (column V.) but with less effect, although the quantity of the former was made as large in the experiment as was consistent with fermentation, and much greater than is ever employed by the brewer. The general mean of these four liquids, all containing starch-sugar, appears in column VI.

The highest degree of original gravity which the sugar-solutions and malt infusions of the preceding Tables possessed before fermentation, was about 1057, but it was desirable to extend the observations to worts of higher gravities. Pale malt worts with hops, which, representing beer, are of most interest, were fermented: they had in two experiments the original gravity 1087·9, and in one experiment 1121, and were frequently examined at different stages, as before, till all fermentation ceased. The three experiments gave

numbers which did not diverge anywhere during their common range more than 0·7 degree of gravity, and at the same time were in harmony with the earlier experiments on pale malt with hops (Table IX.) The mean of the new experiments gave for six degrees of spirit-indication, 24·0 degrees of gravity lost, instead of 23·9 degrees, as in Table IX.; and for 7 degrees of spirit-indication, 28·7 degrees of gravity lost, in the place of 28·4, as in Table IX.

TABLE XII.—MALT-WORT OF HIGH ORIGINAL GRAVITY WITH HOPS.

DEGREES OF SPIRIT-INDICATION WITH DEGREES OF GRAVITY LOST.

Degrees of Spirit-Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0										
1										
2										
3										
4										
5	—	—	—	—	—	—	22·1	22·5	23·0	23·5
6	24·0	24·4	24·9	25·3	25·8	26·2	26·7	27·2	27·7	28·2
7	28·7	29·2	29·6	30·1	30·6	31·1	31·6	32·1	32·6	33·1
8	33·6	34·1	34·7	35·2	35·7	36·2	36·7	37·2	37·7	38·2
9	38·7	39·2	39·8	40·3	40·8	41·3	41·8	42·3	42·8	43·3
10	43·8	44·3	44·9	45·4	45·9	46·4	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·4	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	70·5									

This last Table, combined with Table XI., exhibits the relation between the spirits obtained by distillation from beer, and the degrees of gravity which the original wort loses in producing the spirits, through a range of gravity in the wort, which ascends from 1000 to 1121. It is given in a complete form as Table A, at the end of the Report.

By means of Table A the original gravity of a specimen of beer may therefore be calculated back, and ascertained from the two data which have been specified, namely (1), the degree of spirit-indication which the spirits contained in the beer exhibit, when made up with water to the same measure as the original beer; and (2) the extract gravity of the beer, or the specific gravity of the beer deprived of its spirit, and made up to its original volume with water. A specimen of beer when examined gave the following data :

Spirit-indication . . . 9·9
Extract gravity . . . 1044·7

By Table A, 9·9 degrees of spirit-indication represent 43·7 degrees of gravity lost; which, added to 1044·7, the extract gravity of the same beer, make up 1088·4 degrees, the original gravity of the beer.

The two experimental data required to furnish means of deter-
mining the original gravity of beer, by the process already described,
are obtained with great precision when proper care is taken.   One of
these data, however, namely, the spirit-indication of the beer, involves
the distillation of the beer, and the collection of the whole alcohol
without loss, a delicate process, which it has been attempted to
supersede by operations of less difficulty and nicety.   One of these
operations, long practised by the German brewers, has been examined
and recommended by Balling, and has also been investigated by
Messrs. Dobson and Phillips, under whose notice it appears to have
been first brought as a method which Mr. Stevenson, of Edinburgh,
had suggested and attempted to carry out.

The object is still to obtain the spirit-indication of the beer.   The
specific gravity of the beer is first observed by means of the hydro-
meter or weighing-bottle.   The extract gravity of the beer is next
observed as in the former method; but the beer for this purpose may
be boiled in an open glass flask till the spirits are gone, as the new
process does not require the spirits to be collected.   The spiritless
liquid remaining is then made up to the original volume of the beer as
before.   By losing its spirits, the beer of course always increases in
gravity, and the more so the richer in alcohol the beer has been.
The difference between the two gravities is the new spirit-indication,
and is obtained by subtracting the beer gravity from the extract
gravity, which last is always the higher number.

The data in a particular beer were as follows :—

Extract gravity	1044·7
Beer gravity	1035·1
Spirit-indication	9·6 degrees.

Now the same beer gave by distillation, or the former method, a
spirit-indication of 9·9 degrees.   The new spirit-indication by evapo-
ration is, therefore, less by 0·3 degree than the old indication by
distillation.   The means were obtained of comparing the two indica-
tions given by the same fermented wort or beer in several hundred
cases, by adopting the practice of boiling the beer in a retort, instead
of an open flask or basin, and collecting the alcohol at the same time.
The evaporation uniformly indicated a quantity of spirits in the beer
nearly the same as was obtained by distillation, but always sensibly
less, as in the preceding instance.   These experiments being made
upon fermented liquids of known original gravity, the relation could
always be observed between the new spirit-indication and the degrees
of specific gravity lost by the beer.   Tables of the degrees of spirit-
indication, with their corresponding degrees of gravity lost, were thus
constructed, exactly in the same manner as the Tables which precede ;
and these new Tables may be applied in the same way to ascertain

the original gravity of any specimen of beer. Having found the degrees of spirit-indication of the beer by evaporation, the corresponding degrees of gravity lost are taken from the Table, and adding these degrees to the extract gravity of the beer, also observed, the original gravity is found. Thus the spirit-indication (by the evaporation method) of the beer lately referred to, was 9·6 degrees, which mark 43 degrees of gravity lost in the new Tables. Adding these to 1044·7, the extract gravity of the same beer, 1087·7 is obtained as the original gravity of the beer.

As the numbers of the second set of Tables belonging to the evaporation process, are derived from the same fermentations of cane-sugar starch-sugar, and malt in different conditions, as supplied the first series of Tables, they give the means of forming a strict comparison between the spirit-indications obtained by the two processes.

The want of coincidence between the two sets of Tables requires explanation. The same degrees of gravity lost give less spirit, or, in other words, the same spirits or degrees of spirit-indication always give more degrees of gravity lost in the Evaporation Tables, principally from this circumstance. When alcohol is added to pure water the density of the latter undergoes a certain diminution. By an addition of eight per cent by weight of alcohol the density of water is reduced from 1000 to 986·7, which is a loss of gravity of 13·3 degrees. But eight per cent of alcohol in the same volume as before of water containing ten per cent. of cane-sugar, occasions a loss of gravity of only 12·92 degrees (a fall from 1036·47 to 1023·55). The degrees of spirit-indication obtained are, therefore, less from the same absolute quantity of spirit in the sugar solution than in pure water. Now the sugar solution containing alcohol represents the beer, and gives the loss of gravity which the beer sustains by evaporation. On the other hand, the first mixture of pure water and alcohol represents the dilute spirits obtained from the same beer by distillation. The results here are:

<div align="center">

Degrees of spirit-indication 13·30, by distillation.

,,   ,,   ,,   12·92, by evaporation.

———————

Difference . . 0·38

</div>

It thus appears that alcohol reduces the gravity of a solution of sugar, or we may suppose infusion of malt, not quite so much, by a small quantity, as it reduces the gravity of water. It has hitherto been believed that alcohol has the same effect upon the density of saccharine solutions as upon water, in which case the spirit-indications obtained from beer by the evaporation and distillation methods should necessarily be the same. But it appears from the following series of experiments on the subject, that a sensibly greater condensation always occurs when spirits are mixed with saccharine solutions than with water.

TABLE XIII.—SUGAR DISSOLVED IN SPIRITS,

COMPARED WITH SUGAR DISSOLVED IN EQUAL VOLUMES OF WATER.

Alcohol, in 100 parts of Solvent.	Sugar, added to 100 parts of Solvent.	Specific gravity of Solvent.	Specific gravity of Solution.	Spirit-Indication in Water.	Spirit-Indication in Solution of Sugar.
0	5	1000	1018·83		
2	5	996·35	1015·19	3·65	3·64
4	5	992·80	1011·74	7·20	7·09
6	5	989·63	1008·52	10·37	10·31
8	5	986·76	1005·70	13·24	13·13
10	5	983·91	1002·91	16·09	15·92
12	5	981·23	1000·35	18·77	18·48
0	10	1000	1036·47		
2	10	996·35	1032·90	3·65	3·57
4	10	992·80	1029·49	7·20	6·98
6	10	989·63	1026·31	10·37	10·16
8	10	986·76	1023·56	13·24	12·91
10	10	983·91	1020·77	16·09	15·70
12	10	981·23	1018·23	18·77	18·24
0	15	1000	1053		
2	15	996·35	1049·54	3·65	3·46
4	15	992·80	1046·24	7·20	6·76
6	15	989·63	1043·20	10·37	9·80
8	15	986·76	1040·42	13·24	12·58
10	15	983·91	1037·63	16·09	15·37
12	15	981·23	1035·06	18·77	17·94
0	20	1000	1068·62		
2	20	996·35	1065·26	3·65	3·36
4	20	992·80	1061·99	7·20	6·63
6	20	989·63	1059·06	10·37	9·56
8	20	986·76	1056·31	13·24	12·31
10	20	983·91	1053·52	16·09	15·10
12	20	981·23	1050·82	18·77	17·80

This increased condensation, although small in amount, will be found quite sufficient to account for the difference, amounting to about 1·3 degrees of gravity in the higher numbers, which holds between the gravities lost, corresponding to the same degrees of spirit-indication in the two series of Tables. To obtain the correct original gravity of beer, it is therefore necessary to make use of the proper Table, according as the spirit-indication of the beer has been obtained by the distillation or by the evaporation method. The degrees of gravity lost thus found, are added to the extract gravity, which is the same in both modes of examination.

Although the evaporation process is the easiest in practice, yet it does not appear to admit of the same degree of precision as the distillation process. In two experiments made upon the same beer, a difference of 0·4 or 0·5 degree of original gravity is not unusual with the evaporation, instead of the coincidence almost perfect, which holds

in the repetition of the distillation. It is believed that the imperfect result of the evaporation depends chiefly upon the difficulty of observing with accuracy the specific gravity of a frothing liquid like beer, which is one of the data. The carbonic acid in the beer can have little influence, otherwise, on the result, for it seldom constitutes more than one five-hundredth part of the whole weight of the beer. The gravity of the dissolved carbonic acid appears to exceed a little only that of water, so that although the former is driven off entirely in the boiling, it is replaced afterwards by a liquid (water) of nearly equal density, when the extract gravity is observed. The carbonic acid therefore is reckoned as so much water in the beer.

The Tables of the mean results obtained from the various worts by the evaporation process are now subjoined.

TABLE XIV.—CANE-SUGAR.

DEGREES OF SPIRIT-INDICATION, WITH CORRESPONDING DEGREES OF GRAVITY
LOST.

Degrees of Spirit-Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·2	·4	·6	·8	1·0	1·2	1·4	1·7	2·0
1	2·3	2·6	3·0	3·3	3·7	4·0	4·4	4·7	5·0	5·4
2	5·8	6·1	6·5	6·9	7·3	7·7	8·1	8·5	8·9	9·4
3	9·9	10·4	10·8	11·3	11·7	12·2	12·6	13·1	13·6	14·0
4	14·4	14·8	15·3	15·7	16·2	16·6	17·0	17·4	17·8	18·2
5	18·7	19·1	19·6	20·0	20·4	20·9	21·4	21·9	22·4	22·9
6	23·4	23·8	24·3	24·8	25·2	25·7	26·1	26·6	27·1	27·6
7	28·1	28·5	29·0	29·5	29·9	30·4	30·8	31·3	31·8	32·3
8	32·8	33·3	33·8	34·3	34·8	35·3	35·8	36·3	36·8	37·3
9	37·8	38·3	38·8	39·3	39·8	40·3	40·8	41·3	41·8	42·3
10	42·8	43·3	43·9	44·4	45·0	45·6	46·1	46·7	47·3	47·9
11	48·5									

TABLE XV.—STARCH-SUGAR.

Degrees of Spirit-Indication	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·3	·6	·9	1·2	1·5	1·8	2·2	2·5	2·9
1	3·2	3·6	4·0	4·3	4·7	5·1	5·5	5·9	6·3	6·7
2	7·1	7·5	7·9	8·4	8·8	9·2	9·6	10·0	10·4	10·8
3	11·3	11·7	12·1	12·6	13·0	13·5	13·9	14·3	14·7	15·1
4	15·6	16·0	16·5	16·9	17·4	17·8	18·3	18·7	19·1	19·5
5	20·0	20·4	20·9	21·3	21·8	22·2	22·7	23·2	23·7	24·2
6	24·7	25·1	25·6	26·1	26·6	27·1	27·6	28·1	28·6	29·1
7	29·7	30·0	30·5	31·0	31·5	32·0	32·5	33·0	33·5	34·0
8	34·4	34·9	35·5	36·0	36·5	37·1	37·6	38·1	38·6	39·1
9	39·6	40·2	40·7	41·2	41·7	42·3	42·8	43·3	43·8	44·3
10	44·8	45·3	45·9	46·4	47·0	47·5	48·0	48·6	49·1	49·6

TABLE XVI.—MALT WORT WITHOUT HOPS.

Degrees of Spirit Indication	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·3	·7	1·1	1·5	1·9	2·3	2·7	3·1	3·5
1	3·9	4·3	4·7	5·1	5·5	5·9	6·3	6·7	7·1	7·5
2	8·0	8·4	8 8	9·2	9·6	10·0	10·4	10·8	11·2	11·6
3	12·0	12·4	12·9	13·3	13·7	14·2	14·6	15·0	15·4	15·8
4	16·3	16·7	17·1	17·5	18·0	18·4	18·8	19·2	19·6	20·0
5	20·5	21·0	21·4	21·9	22·3	22·8	23·2	23·7	24·1	24·5
6	25·0	25·4	25·9	26·4	26·9	27·3	27·8	28·3	28·8	29·3
7	29·8	30·3	30·8	31·3	31·8	32·3	32·8	33·3	33·8	34·2
8	34·8	35·4	36·0	36·6	37·2	37·8	38·4	39·0	39·6	40·2
9	40·8									

TABLE XVII.—MALT WORT WITH HOPS.

Degrees of Spirit-Indication	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·3	·6	·9	1·2	1·5	1·8	2·1	2.4	2·7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·3
2	6·7	7·2	7·6	8·0	8·4	8·8	9·2	9·6	10·0	10·4
3	10·8	11·2	11·7	12·1	12·6	13·0	13·4	13·8	14·2	14·6
4	15·0	15·4	15·9	16·3	16·8	17·2	17·7	18·1	18.6	19·0
5	19·4	19·8	20·3	20·7	21·2	21·6	22·1	22·5	22·9	23·3
6	23·8	24·2	24·7	25·1	25·6	26·0	26·5	26·9	27·4	27·8
7	28·3	28·7	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7
8	33·2									

TABLE XVIII.—BROWN AND PALE MALT WORTS.

Degrees of Spirit-Indication	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·3	·7	1·0	1·4	1·8	2·2	2·6	3·0	3·4
1	3·8	4·2	4·6	5·0	5·4	5·8	6·2	6·6	7·1	7·5
2	7·9	8·3	8·8	9·2	9·6	10·0	10·4	10·8	11·2	11·6
3	12·0	12·4	12·9	13·3	13·7	14·1	14·5	15·0	15·4	15·8
4	16·2	16·6	17·0	17·5	17·9	18·4	18·8	19·3	19·7	20·1
5	20·5	20·9	21·4	21·8	22·3	22·7	23·2	23·6	24·1	24·6
6	25·0	25·4	25·9	26·3	26·8	27·2	27·7	28·2	28·7	29·1
7	29·6	30·0	30·5	30·9	31·4	31·9	32·3	32·8	33·3	33·8
8	34·4									

TABLE XIX.—VARIOUS WORTS: Mean of Tables XV., XVI., XVII, and XVIII.

Degrees of Spirit-Indication	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
	—	·3	·7	1·0	1·4	1·7	2·1	2·4	2·8	3·1
1	3·5	3·8	4·2	4·6	5·0	5·4	5·8	6·2	6·6	7·0
2	7·4	7 8	8·2	8·7	9·1	9·5	9 9	10·3	10·7	11·1
3	11·5	11·9	12·4	12·8	13·2	13 6	14·0	14·4	14·8	15·3
4	15·8	16 2	16·6	17·0	17·4	17·9	18·4	18·8	19·3	19·8
5	20·1	20·5	21·0	21·4	21·9	22·3	22·8	23·2	23·7	24·1
6	24·6	25·0	25·5	26·0	26·4	26·9	27·3	27·8	28·3	28·8
7	29·3	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2	33·7
8	34·2	34·7	35·3	35·9	36·5	37·1	37·7	38·3	38·9	39·5
9	40·1									
10	44 8									

TABLE XX.—MEAN OF TABLES XV., XVI., XVII., and XVIII.

	1	2	3	4	5	6	7	8	9	10
No. xv.	3·2	7·1	11·3	15·6	20·0	24·7	29·6	34·4	39·6	44·8
xvi.	3·9	8·0	12·0	16·3	20·5	25·0	29·8	34·8	40·8	
xvii.	3·0	6·7	10·8	15·0	19·4	23·8	28·3	33·2		
xviii.	3·8	7·9	12·0	16·2	20·5	25·0	29·6	34·4		
Mean	3·5	7·4	11·5	15·8	20·1	24·6	29·3	34·2	40·2	

TABLE XXI.—MALT WORT OF HIGH ORIGINAL GRAVITY WITH HOPS.

Degrees of Spirit-Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0										
1										
2										
3										
4										
5	21·0	21·4	21·9	22·3	22·8	23·2	23·7	24·1	24·6	25·0
6	25·4	25·9	26·3	26·8	27·3	27·8	28·2	28·7	29·1	29·6
7	30·0	30·5	30·9	31·4	31·9	32·3	32·8	33·3	33·8	34·3
8	34·8	35·3	35·8	36·3	36·8	37·3	37·8	38·3	38·8	39·3
9	39·8	40·3	40·8	41·4	41·9	42·4	43·0	43·5	44·0	44·5
10	45·0	45·5	46·1	46·6	47·2	47·7	48·2	48·7	49·3	49·8
11	50·3	50·9	51·4	51·9	52·5	53·0	53·5	54·0	54·5	55·0
12	55·6	56·2	56·7	57·3	57·8	58·3	58·9	59·4	59·9	60·5
13	61·0	61·6	62·1	62·7	63·2	63·8	64·3	64·9	65·4	66·0
14	66·5	67·0	67·6	68·1	68·7	69·2	69·8	70·4	70·9	71·4
15	72·0									

In the examination of fermented liquids, the acetic acid present should not be overlooked, as the influence of this constituent upon the original gravity of some kinds of beer, particularly old and hard beer, is often considerable. There is, however, a certain amount of acid present in all healthy fermentations, and this, in the experiments on which our tables have been founded, was estimated at one part of absolute acetic acid ($C_4 H_4 O_4$) in one thousand parts of wort. Any excess of acid beyond this should be ascertained by neutralizing the beer by an alkaline test-solution. Sixty parts (one equivalent) of acetic acid, represent forty-six parts of absolute alcohol; a proportion by which the weight of alcohol, which has disappeared in the formation of acetic acid, is calculated. This corresponding weight of alcohol has a certain spirit-indication, which is to be added to the spirit-indication of the beer itself before the degrees of gravity lost are taken from the table. The calculated original gravity of old beers is often thus very sensibly increased.

The Tables for calculating original gravities, constructed by Messrs. Dobson and Phillips, were deduced by these gentlemen from observations made upon several different saccharine solutions of known original gravity submitted to fermentation, and are the same in principle as the Tables given in this Report. The old observations appear to have been made with the greatest care and accuracy, and the Table founded upon them, which has been used by the Excise for some time,

is almost identical with Table A, in the Appendix, which we now give as the result of the more numerous and varied experiments subsequently instituted during the present inquiry.

The process of Professor Balling, of Prague, for ascertaining original gravities, forms a part of a general method of analyzing beer which the author has developed in his great work upon Brewing.* The method is remarkable for the number of valuable results which are deduced by calculation from simple observations of the physical properties of the beer, chiefly made by means of the saccharometer. The chemical properties of the extractive matter are not investigated, and the source of the anomalies in the densities of fermented liquids are, therefore, left in the dark. But a certain number of observations have been made on the relation and dependence of the densities of the worts, alcohol, and extractive matter, of particular fermented liquids. These observations afford empirical data for reaching the original gravity, by means of a process of calculation, which is highly remarkable for its ingenuity and success, considering the limited knowledge of the actual chemical changes involved in fermentation. In several samples of beer, to which the formula of Balling was applied by us, it was found to give an original gravity within a single degree of the truth.

Every facility and assistance in pursuing the necessary inquiries respecting fermentation on a large scale were afforded to us by the trade, and we have much pleasure in acknowledging our obligations both to the partners and principal officers of the houses of Messrs. Abbott and Son; Combe, Delafield, and Co.; Furze and Son; Reid and Co.; Thorne and Co.; Truman, Hanbury and Buxton, and Whitbread and Co., of London; and to Messrs. Allsopp and Sons, and Bass and Co., of Burton. We thus obtained the means of verifying the correctness of the original gravities calculated from our tables by means of specimens of beer, of which the original gravity of the worts had been noted with sufficient accuracy, and which had been preserved for a considerable length of time. A series of experiments which had been made by Mr. Crockford, of the Long Acre Brewery, expressly with a view of illustrating the subject of original gravities, and which he placed without reserve at our disposal, and also a long series of most careful observations made by Mr. Bottinger in Messrs. Allsopp's brewery, were particularly pertinent to the inquiry, and afforded a satisfactory confirmation of the sufficiency of the methods.

The methods of determining original gravities already described are essentially empirical. But the investigations respecting the nature of the process of fermentation, into which they have led,

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* *Die Gährungschemie wissenschaftlich begründet und in ihrer Anwendung auf die Weinbereitung, Bierbrauerei, Branntweinbrennerei und Hefenerzeugung praktisch dargestellt*, von Carl J. N. Balling. Prague, 1845. Or a shorter treatise by the same author—*Die Saccharometrische Bier-und Branntweinmeischprobe*. Prague, 1846.

suggested the principle upon which the rational process should be founded, and which deserves to be explained for the better illustration of the subject. This process is chiefly interesting in a scientific point of view, as it is too operose and delicate in the form in which it can be at present offered, to supersede the preceding methods which are recommended for practice.

The fact has already been insisted upon, that the alcohol obtained from beer represents a perfectly definite quantity of starch-sugar and nothing else; and so furnishes a portion of the original gravity which is clear and indisputable. The difficulty is with that portion of the original gravity which is represented by the solid matter remaining in the beer. Here also the difficulty would vanish, if that solid matter were either all starch-sugar (which it never is), or entirely composed of the extractive matter already described, as frequently occurs in old hard beer. The gravities of solutions of starch-sugar, and of the extractive matter are different, but are now both fully known. If the solid matter of the beer consisted entirely of the former substance, then the original gravity of the beer would be that of the joint amount of the starch-sugar actually found in the beer, and of that represented by the alcohol of the beer, the whole quantity of sugar being dissolved in water, and having the original volume of the beer. The only further information required might be obtained from a Table of the gravities of solutions of starch-sugar. The specific gravity thus found of the solution of starch-sugar in question, represents the original gravity of the beer.

On the second supposition, that the solid matter of the beer was all extractive matter (without sugar), then the reference should be made to a table of the specific gravities of solutions of different proportions of that substance, such as Table V., page 236, but more extended. In a parallel column the gravities of solutions of starch-sugar possessing the same quantity of carbon as the extractive and corresponding to it, would be placed, and in another column the quantities of starch-sugar in the former solutions of that substance. Such a Table would give at once, therefore, the quantity of starch-sugar corresponding to the extractive, and adding the quantity of starch-sugar represented by the alcohol of the beer, the entire quantity of starch-sugar becomes known, and the original gravity is found from it as in the preceding case.

The problem, therefore, may be solved in the two extreme conditions of the beer which have been supposed. The real difficulty is with the intermediate condition, which is also the most frequent one, where the solid matter of the beer is partly starch-sugar and partly extractive; for no accurate chemical means are known of separating these substances, and so determining the quantity of each in the mixture.

But a remedy presented itself. The fermentation of the beer was completed by the addition of yeast, and the constituents of the beer were thus reduced to alcohol and extractive only, from which the original gravity, as is seen, can be calculated.

For this purpose a small but known measure of the beer, such as four fluid ounces, was carefully deprived of spirits by distillation, in a glass retort. To the fluid, when cooled, a charge of fresh yeast, amounting to 150 grains, was added, and the mixture kept at 80° for a period of sixteen hours. Care was taken to connect the retort, from the commencement, with a tube condenser, so that the alcoholic vapour which exhaled from the wash during fermentation should not be lost. When the fermentation had entirely ceased, heat was applied to the retort to distil off the alcohol; which was collected in a cooled receiver. About three-fifths of the liquid were distilled over for this purpose; and the volume of the distillate was then made up with water to the original volume of the beer. The specific gravity of the last spirituous liquid was now taken, by the weighing bottle. To obtain a correction for the small quantity of alcohol unavoidably introduced by the yeast, a parallel experiment was made with that substance. The same weight of yeast was mixed with water, and distilled in another similar retort. The volume of this second distillate was also made up by water to the beer volume; its specific gravity observed, and deducted from that of the preceding spirituous liquid. This alcohol was added to that obtained in the first distillation of the beer, and the weight of starch-sugar corresponding to the whole amount of alcohol was calculated. This was the first result.

For the solid matter of the beer : the spiritless liquid remaining in the retort was made up with water to the beer volume, and the specific gravity observed. A correction was also required here for the yeast, which is obtained, by making up the water and yeast, distilled in the second retort, to the original volume of the beer, and deducting the gravity of this fluid from the other. The quantity of starch-sugar corresponding to this corrected gravity of the extractive matter was now furnished by the Table, this was the second result.

The two quantities of starch-sugar thus obtained were added together. The specific gravity of the solution of the whole amount of starch-sugar, as found in the Table, represented the original gravity of the beer.

This method must give an original gravity slightly higher than the truth, owing to the circumstance that the dextrin, albumen, and salts, which are found among the solid matters dissolved in beer, are treated as having the low gravity of extractive matter, and accordingly amplified by about one-sixth, like that substance, in allowing for them ultimately as starch-sugar. The error from this source, however, is inconsiderable. It is to be further observed, that the error from imperfect manipulation, of which there is most risk in the process, is leaving a little sugar in the extractive matter from incomplete fermentation. This accident also increases the original gravity deduced. The process has given results which are remarkably uniform, and is valuable in the scientific investigation of the subject, although not of that ready and easy execution which is necessary for ordinary practice, and which recommends the former method. That

method, in its two modifications, has been sufficiently described in the preceding pages, and it now only remains to append the Tables required for its application, which embody the general result of the inquiry.

TABLE A.—To be used in ascertaining Original Gravities by the DISTILLATION PROCESS.

DEGREES OF SPIRIT-INDICATION WITH CORRESPONDING DEGREES OF GRAVITY LOST IN MALT WORTS.

Degrees of Spirit-Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·2	·6	·9	1·2	1·5	1·8	2·1	2·4	2·7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·8	14·2	14·7
4	15·1	15·5	16·0	16·4	16·8	17·3	17·7	18·2	18·6	19·1
5	19·5	19·9	20·4	20·9	21·3	21·8	22·2	22·7	23·1	23·6
6	24·1	24·6	25·0	25·5	26·0	26·4	26·9	27·4	27·8	28·3
7	28·8	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2
8	33·7	34·3	34·8	35·4	35·9	36·5	37·0	37·5	38·0	38·6
9	39·1	39·7	40·2	40·7	41·2	41·7	42·2	42·7	43·2	43·7
10	44·2	44·7	45·1	45·6	46·0	46·5	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·4	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	70·5									

TABLE B.—To be used in ascertaining Original Gravities by the EVAPORATION PROCESS.

DEGREES OF SPIRIT-INDICATION WITH CORRESPONDING DEGREES OF GRAVITY LOST IN MALT WORTS.

Degrees of Spirit-Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·3	·7	1·0	1·4	1·7	2·1	2·4	2·8	3·1
1	3·5	3·8	4·2	4·6	5·0	5·4	5·8	6·2	6·6	7·0
2	7·4	7·8	8·2	8·7	9·1	9·5	9·9	10·3	10·7	11·1
3	11·5	11·9	12·4	12·8	13·2	13·6	14·0	14·4	14·8	15.3
4	15·8	16·2	16·6	17·0	17·4	17·9	18·4	18·8	19·3	19·8
5	20·3	20·7	21·2	21·6	22·1	22·5	23·0	23·4	23·9	24·3
6	24·8	25·2	25·6	26·1	26·6	27·0	27·5	28·0	28·5	29·0
7	29·5	30·0	30·4	30·9	31·3	31·8	32·3	32·8	33·3	33·8
8	34·3	34·9	35·5	36·0	36·6	37·1	37·7	38·3	38·8	39·4
9	40·0	40·5	41·0	41·5	42·0	42·5	43·0	43·5	44·0	44·4
10	44·9	45·4	46·0	46·5	47·1	47·6	48·2	48·7	49·3	49·8
11	50·3	50·9	51·4	51·9	52·5	53·0	53·5	54·0	54·5	55·0
12	55·6	56·2	56·7	57·3	57·8	58·3	58·9	59·4	59·9	60·5
13	61·0	61·6	62·1	62·7	63·2	63·8	64·3	64·9	65·4	66·0
14	66·5	67·0	67·6	68·1	68·7	69·2	69·8	70·4	70·9	71·4
15	72·0									

The Tables to be used for liquids fermented from cane-sugar and for liquids fermented from starch-sugar, are given at pages 242—3 of the Report for the distillation process, and at page 250 for the evaporation process.

Researches on some of the Crystalline Constituents of Opium.[*]

By Thomas Anderson, M.D., F.R.S.E.

(Abstracted by the Author.)

Opium has been already submitted to investigation by so many chemists, that it may at first sight appear to be an almost exhausted subject; but when we inquire more minutely into its history, the meagre and often conflicting statements of different observers sufficiently indicate the necessity of more extended and minute inquiries, before our knowledge of it can be considered as either definite or satisfactory. No less than ten[†] basic and indifferent substances have been extracted from it; and of these, the constitution of four only, namely, morphine, codeine, papaverine, and narcotine, has been satisfactorily established. Of the remaining six, porphoroxine is still unanalysed; opianine is of recent discovery, and its composition still doubtful; while the formulæ attributed to thebaine, pseudomorphine, narceine, and meconine, are founded on old analyses, made soon after their discovery, at a time when the methods of organic analysis were comparatively imperfect, and certainly cannot be looked upon as very satisfactory.

For the preparation of the bases which form the subject of the following paper, I have made use of the black mother-liquor of the preparation of muriate of morphine, by the process of Robertson and Gregory. This fluid, which is perfectly black, and of the consistence of tar, is diluted with water, and filtered for the separation of a small quantity of flocky substance which deposits. Ammonia is then added as long as a precipitate is obtained, which is separated by filtration through cloth, and subjected to strong pressure. The precipitate thus obtained is dark-coloured and granular, but if left in the press for any length of time, is apt to run into a resinous mass. It must therefore be rapidly removed, broken up with a small quantity of water, and again expressed; and this is repeated several times. The precipitate contains narcotine, along with a considerable quantity of resin, and a small quantity of thebaine. The fluid contains narceine, and must be preserved for its preparation.

A portion of the precipitate is boiled with rectified spirit, and filtered hot; on cooling, impure and highly-coloured crystals of narcotine are deposited, which are collected on a cloth, washed with a small quantity of alcohol, and expressed; the mother-liquor of these crystals is employed for the solution of another quantity of the precipitate, and so on until the whole has been dissolved. The impure crystals of narcotine are then rubbed up with a small quantity of a strong solution of potash, and after standing for some time, washed

[*] Trans. Royal Society, Edinburgh, XX, [3], 347.

[†] Since this paper was written, two new substances have been added to the constituents of opium; these are, the methylonarcotine and propylonarcotine of Wertheim.

with water, and finally crystallised several times from boiling spirit. The alcoholic solution from which the first dark-coloured crystals of narcotine are deposited, on being distilled in the water-bath, leaves behind a dark amorphous mass, containing much resin, mixed with a little narcotine, and the whole of the thebaine contained in the original precipitate. It is treated with hot dilute acetic acid, which dissolves the bases and a small quantity of resin. To this solution subacetate of lead is added until it acquires a distinctly basic reaction, when the whole of the narcotine and resin are deposited, and the thebaine remains in solution. The fluid is filtered from the precipitate, the excess of lead thrown down by sulphuric acid, the sulphate of lead separated by filtration, and the thebaine precipitated by ammonia. The washed precipitate is then dissolved in boiling alcohol, and treated with animal charcoal, and on cooling, the fluid becomes filled with shining plates, which are purified by several crystallisations.

The mother-liquor of the original ammonia-precipitate contains narceine, which is obtained in the following manner. A solution of acetate of lead is added to the fluid, and the dirty brownish precipitate formed, separated by filtration. The excess of lead is separated by sulphuric acid, and the fluid, saturated with ammonia, is set to evaporate at a moderate temperature. When it has reached a certain degree of concentration, a film appears on the surface, and on cooling a quantity of crystalline matter is deposited, which becomes more abundant on being allowed to stand for some days. This substance is collected on a cloth and washed with water, and is then sometimes quite colourless, but has more frequently a somewhat brown colour. It is then boiled with a large quantity of water, and filtered hot ; and on cooling, the fluid becomes filled with fine silky crystals of narceine, which are separated from traces of sulphate of lime by solution in alcohol, and after boiling with animal charcoal and resolution in water are pure.

NARCEINE.

Narceine has been already analysed, both by Pelletier and Couerbe; and from their results the former has deduced the formula $C_{32} H_{24} NO_{16}$, the latter $C_{28} H_{20} NO_{12}$, which, though agreeing tolerably well with their analytical results, are unsupported by determination of the atomic weight, which neither of them appear to have attempted, owing to the impression they derived from their experiments, that narceine is incapable of entering into combination with acids. My own experiments give for it the formula :

$$C_{46} H_{29} NO_{18}$$
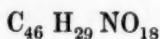
which was substantiated by the analysis of its platinum compound,

which was found to contain 14·56 per cent of platinum, and gave for the atomic weight of the base 464·8, while the theoretical number is 463.

Narceine crystallises in delicate silky needles, which mat together into a bulky mass.   These crystals are always extremely white; and narceine is remarkable for the facility with which it is obtained colourless.   In cold water it is sparingly, and in hot water readily soluble, and the solution on cooling becomes filled with a network of bulky crystals.   It is more soluble in alcohol, and insoluble in ether. Ammonia and dilute solutions of potash and soda dissolve it in larger proportion than water; but the addition of a large quantity of concentrated potash precipitates it, even from a hot solution, in the form of an oily mass, which remains fluid for some time under the solution. When boiled with dilute nitric acid, the fluid acquires a yellow colour, and on saturation with potash, the odour of a volatile base is evolved. Concentrated nitric acid acts violently in the cold, and oxalic acid is found in the solution.   Strong sulphuric acid dissolves it in the cold with an intense red colour, which passes into green on the application of heat.   Strong hydrochloric acid dissolves it entirely, without producing the blue colour described by Pelletier as characteristic of narceine.   I did obtain a blue colour on one occasion, but it was when operating on an impure specimen, and I have never succeeded in obtaining it again; I have been equally unsuccessful with a specimen obtained directly from the establishment of Robiquet, Pelletier and Caventou.   This specimen differed in some respects from that which I had myself prepared, and a single analysis gave results corresponding with the formula $C_{32} H_{19} NO_{10}$; but I have no means of confirming its correctness, as the high price of the material deterred me from further experiments.

Hydrochlorate of Narceine is obtained sometimes in large groups of radiated needles, and sometimes in the form of short thick irregular prisms.   They are soluble in both water and alcohol, and possess a distinctly acid reaction.   Dried at 212° F., they have the formula $C_{46} H_{29} NO_{18} \cdot H Cl$.

Sulphate of Narceine is deposited in tufts of silky needles, not differing much in appearance from the base itself.   It is rather sparingly soluble in cold water, readily in hot.

Nitrate of Narceine is deposited in radiated groups from its hot solution.   It is rather sparingly soluble in the cold.

Chloride of Platinum and Narceine.—When a solution of chloride of platinum is added to hydrochlorate of narceine, the double compound makes its appearance, sometimes as a crystalline powder, sometimes in small prismatic crystals.   Their formula is $C_{46} H_{29} NO_{18} \cdot HCl \cdot Pt Cl_2$.

THEBAINE.

Three different formulæ have been given for thebaine by Pelletier, Couerbe and Kane. They are:

$$\begin{array}{lll}
\text{Pelletier} & . & . & C_{34}\ H_{18}\ NO_6 \\
\text{Couerbe} & . & . & C_{25}\ H_{13\cdot5}\ NO_4 \\
\text{Kane} & . & . & C_{25}\ H_{14}\ NO_3
\end{array}$$

The atomic weight has been determined by the two latter chemists by ascertaining the quantity of hydrochloric acid gas absorbed by the base; Couerbe found 100 parts to absorb 8·35 of acid, while Kane found it to absorb at 212° F., 16·96 per cent, and at ordinary temperatures, 33·28. These results are very nearly in the proportion of 1, 2 and 4; but no reliance can be placed upon them, as I have found that thebaine is very readily decomposed by hydrochloric acid, and none of them agree with the atomic weight deduced from my own experiments. My analysis gives for it the formula:

$$C_{38}\ H_{21}\ NO_6$$
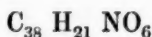
differing from that of codeine by two equivalents of carbon.

Thebaine crystallises from its alcoholic or ethereal solution in brilliant square plates having a silvery lustre. It is insoluble in water, but very soluble in alcohol or ether, especially on boiling. It dissolves readily in acids, and forms salts which are not obtained in crystals from aqueous solutions. It is insoluble in potash and ammonia. Strong sulphuric acid reacts upon it, and produces a deep-red colour, even when it is free from nitric acid. Concentrated nitric acid acts violently in the cold, with copious evolutions of red fumes, and formation of a yellow solution, which becomes dark-coloured on the addition of potash, and evolves a volatile base. In hydrochloric acid it dissolves readily, and the solution on evaporation becomes dark-coloured, and leaves behind a resinous matter, which does not dissolve completely in water. Sulphuric acid, of specific gravity 1·300, dissolves it in the cold; and on gently heating, a resinous or semi-solid matter is thrown down, which, on boiling with water, slowly dissolves, and deposits, on cooling, a rather sparingly soluble salt, in microscopic crystals, which appears to be a product of decomposition, but of which I must defer the examination, until I have obtained an additional quantity of thebaine. Chlorine and bromine rapidly decompose thebaine with the formation of resinous compounds.

Hydrochlorate of Thebaine.—In order to prepare this salt, thebaine is mixed with a small quantity of strong spirit and an alcoholic solution of hydrochloric acid added, until the thebaine is dissolved, an excess being avoided, and on standing, the salt is deposited in fine rhomboidal crystals. They are very soluble in water, and the solu-

tion, on evaporation, yields only a resinous mass. In alcohol, especially if absolute, they are rather sparingly soluble, and in ether they are insoluble. Dried at 212° F., their formula is $C_{38} H_{21} NO_6 . HCl + 2HO$.

Platinochloride of Thebaine is thrown down as a yellow crystalline powder on the addition of chloride of platinum to the preceding compound. It is sparingly soluble in hot water, and the solution on cooling, deposits a salt which appears to be a product of decomposition. The formula of the salt dried at 212° is $C_{38} H_{21} NO_6 . HCl. Pt Cl_2 + 2HO$.

Sulphate of Thebaine is obtained by adding sulphuric acid to an ethereal solution of thebaine, partly in crystals, partly as a resinous mass, becoming crystalline on standing. The hydrochlorate gives with corrosive sublimate, a fine, white, crystalline precipitate of a double salt, and the base itself gives a bulky precipitate; but neither of these substances could be obtained of constant composition. Terchloride of gold gives an orange-yellow precipitate, which fuses at 212° into a resinous mass.

ACTION OF NITRIC ACID ON NARCOTINE.

When concentrated nitric acid is added to narcotine, a very violent action ensues; even in the cold, red fumes are copiously evolved, and a thick, resinous-looking red matter is left behind. With somewhat weaker acid and a gentle heat, a similar action takes place, and a red fluid is obtained, which, by evaporation, yields an amorphous orange residue. In both cases, the action was much too violent, and the product obtained obviously the result of several complex actions. The action of nitric acid in a more dilute state was therefore tried, and after several experiments, the following was found to be the most advantageous method of treatment. Six hundred grains of narcotine are mixed with $2\frac{1}{2}$ ounces, by measure, of nitric acid, of specific gravity 1·400, diluted with ten ounces of water, and exposed in the water-bath to an uniform temperature of 120° Fahr. The narcotine fuses into a yellowish mass, which, by continuous agitation, slowly dissolves without the evolution of red fumes. When the solution is nearly complete, a small quantity of a white deposit begins to make its appearance in the solution, and gradually increases in quantity until the fluid becomes filled with bulky crystalline flocks. The quantity of this substance produced appears to depend, to a great extent, upon the rapidity of the oxidation, being sometimes extremely minute, and always bearing a very small proportion to the quantity of narcotine employed. When these flocks have ceased to increase in quantity, they are separated from the fluid by filtration through asbestos, washed with water, in which they are insoluble, and purified by solution in a considerable quantity of boiling alcohol.

To this substance I give the name of *Teropiammon*. As thus

obtained, it is in the form of very small colourless needles, insoluble in water; sparingly soluble in cold, and more soluble in boiling alcohol. It is little soluble in ether. Concentrated sulphuric acid dissolves it in the cold, and the solution, which is yellow, gives a fine crimson on being heated. Nitric acid decomposes it. Hydrochloric acid and ammonia have no action on it. Boiled with potash, ammonia is evolved, and opianic acid is found in the solution. I at first considered it identical with Wöhler's opiammon, but the absence of xanthopenic acid in this reaction, and various other differences, convinced me that it was not the same, and this was confirmed by analysis, which gave for it the formula $C_{60} H_{29} NO_{26}$. That it is actually different from Wöhler's opiammon, of which the formula is $C_{40} H_{19} NO_{16}$, is very obvious, but it bears an interesting relation to it. The latter substance is derived from two equivalents of opianic acid and one equivalent of ammonia, by the removal of the elements of four equivalents of water as thus represented :

$$
\begin{array}{ll}
\text{2 eq. opianic acid} & C_{40} H_{20} \quad O_{20} \\
\text{1 eq. ammonia} & \quad\; H_3 \; N \\
\hline
& C_{40} H_{23} \; N \; O_{20} \\
\text{4 eq. water} & \quad\; H_4 \qquad O_4 \\
\hline
\text{1 eq. opiammon} & C_{40} H_{19} \; N \; O_{16}
\end{array}
$$
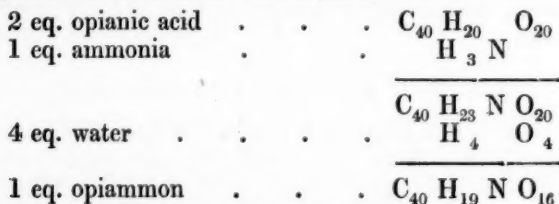
and the new compound is derived in a precisely similar manner from three equivalents of opianic acid :

$$
\begin{array}{ll}
\text{3 eq. opianic acid} & C_{60} H_{30} \quad O_{30} \\
\text{1 eq. ammonia} & \quad\; H_3 \; N \\
\hline
& C_{60} H_{33} \; N \; O_{30} \\
\text{4 eq. water} & \quad\; H_4 \qquad O_4 \\
\hline
\text{1 eq. teropiammon} & C_{60} H_{29} \; N \; O_{26}
\end{array}
$$
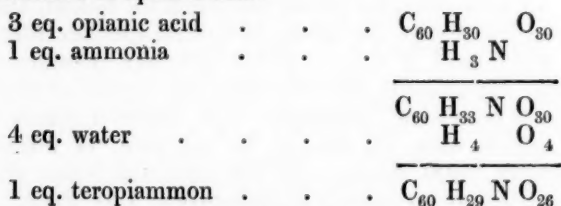
Both these substances, therefore, are produced in a similar manner from different opianates of ammonia; and it is in consideration of this constitution that I give to my compound the name of *teropiammon*, while I should propose that of *binopiammon* for Wöhler's substance, and leave the name of *opiammon* for the compound similarly obtained from a single equivalent of opianic acid, should it ever be discovered. The production of teropiammon in a highly acid fluid is a very remarkable phenomenon, and one, so far as I know, of which we have no other example. It is obviously the result of a secondary action, but it has appeared to me that it was most abundantly produced when the action of the nitric acid was most moderate, and I have never succeeded in obtaining it in larger quantity by continuing the action further.

The fluid from which teropiammon has been separated is yellow, and on supersaturation with potash, deposits a crystalline powder. This was found to be cotarnine, which can be obtained in this way much more readily than by Wöhler's process.

In the alkaline fluid from which the cotarnine had been separated, it was natural to look for opianic acid, and its presence was soon established, as well as that of hemipinic acid, and another substance, which I call *Opianyl*. These substances were not, however, invariably all present, opianic acid and opianyl being sometimes entirely absent, and the latter being only found when the conditions of the oxidation were very successfully fulfilled. To obtain these substances, the alkaline fluid is evaporated to a small bulk and the crystals of nitre which form are separated. The syrupy mother-liquor is treated with alcohol, to separate carbonate of potash, the alcohol distilled off, and hydrochloric acid added to the cold residue, when there is obtained a precipitate containing opianic and hemipinic acids and opianyl.

OPIANYL.

This substance is only formed when the oxidation has been extremely gentle, and, though repeated trials have been made, it has been found impossible to moderate the action in such a way as to produce it at will. In order to obtain it in a pure state, the precipitate by hydrochloric acid, which has just been referred to, is dissolved in a large quantity of boiling water, and the solution allowed to cool. A crop of crystals is deposited which consists of opianyl along with some opianic acid, if the quantity of water employed has not been sufficiently large. These crystals are purified by solution in boiling water and in alcohol. In one instance, opianyl was obtained along with hemipinic acid, and with only traces of opianic acid; and in that case, its purification was conveniently effected by dissolving in boiling water, precipitating hemipinate of lead with a solution of neutral acetate of lead, washing the precipitate in boiling water, and evaporating to a small bulk, when opianyl deposited in colourless crystals, which were purified by solution in boiling water.

Opianyl is thus obtained in long, colourless needles, which are sparingly soluble in cold, more so in hot water. When boiled with a quantity of water insufficient to dissolve it, it melts under the fluid, but when dry it requires a temperature of 230° Fahr. to produce its fusion, and resolidifies at 220°. It dissolves both in alcohol and ether. Sulphuric acid dissolves it in the cold, and the colourless solution acquires a fine and characteristic purple colour on heating. Boiling nitric acid decomposes it. It is not more soluble in potash, soda, and ammonia than in water, and forms no compounds with the metallic oxides. Its analysis gave results corresponding to the formula

$$C_{20} \ H_{10} \ O_8.$$

Opianyl thus bears an interesting relation to opianic and hemipinic acids, provided we assume for the former the formula as corrected by Berzelius, and, for the latter, an atomic weight twice as high as that assigned to it by Wöhler, both of which are consistent with my analyses. The three substances then stand as follows:

Opianyl . . . . $C_{20} H_{10} O_8$
Opianic acid . . . $C_{20} H_{10} O_{10}$
Hemipinic acid . . $C_{20} H_{10} O_{12}$

and appear as three successive degrees of oxidation of the same radical.

The derivation of opianyl from narcotine is abundantly simple. Two equivalents of hydrogen are oxidised by the nitric acid, and the narcotine splits up into opianyl and cotarnine, as thus expressed:

$$C_{46} H_{25} NO_{14} + O_2 = C_{26} H_{13} NO_6 + C_{20} H_{10} O_8 + 2HO.$$

$\underbrace{\phantom{C_{46} H_{25} NO_{14}}}_{\text{Narcotine.}}$ $\underbrace{\phantom{C_{26} H_{13} NO_6}}_{\text{Cotarnine.}}$ $\underbrace{\phantom{C_{20} H_{10} O_8}}_{\text{Opianyl.}}$
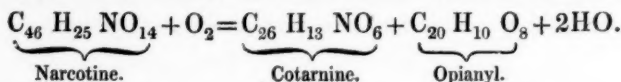
The same scheme, with the addition of two or four equivalents of oxygen, represents also the mode in which opianic and hemipinic acids respectively are derived from narcotine much more simply than it has been by Blyth, in his paper on the action of bichloride of platinum on narcotine, who gives a scheme involving the evolution of carbonic acid. The appearance of this gas, which was actually observed by Blyth during the action, has, however, always appeared to me to be the result of a secondary decomposition; and this view, I think, receives confirmation from the production of teropiammon, where nitric acid acts even in the most feeble manner on narcotine, and the formation of which must, of necessity, be attended by the evolution of carbonic acid.

If we pursue the relations of opianyl to narcotine, we shall find that these also are of a very interesting nature. By subtracting an equivalent of cotarnine from one of narcotine,

Narcotine . . . . $C_{46} H_{25} NO_{14}$
Cotarnine . . . . $C_{26} H_{13} NO_6$
_____
$C_{20} H_{12} O_8$
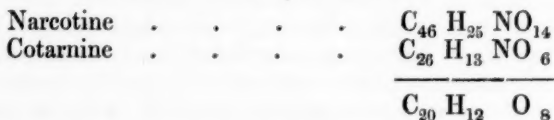
we find that the substance coupled with cotarnine to form narcotine may be considered as a *hydruret* of opianyl, or a substance bearing to opianyl a relation similar to that which alloxantin bears to alloxan, and the preparation of which, in a separate form, would be most interesting. The attempts which I have made to obtain it have, however, as yet proved abortive. I have tried the action of sulphuretted hydrogen upon opianyl, but no change took place, and also the fer-

mentation of narcotine, but with equally little success.   It is possible that Wöhler's sulphopianic acid $C_{20} H_{10} O_8 + S_2$, may have some relations with this substance, and in this point of view deserves a more extended examination.

Hydrate of Opianyl.—On one occasion I obtained by acting on narcotine, a substance similar in most of its properties to opianyl, but which fused at 205° F.   Its analysis corresponded to a hydrate of that substance $C_{20} H_{10} O_8 + HO$, but I did not again obtain it, and I had not enough for a detailed examination.

Opianic Acid is obtained by evaporating the fluid which has deposited opianyl.   I have repeated its analysis for the purpose of fixing its formula, and the results agree with $C_{20} H_{10} O_{10}$, the quantity of hydrogen being much too high for Wöhler's formula, $C_{20} H_9 O_{10}$, although every care was taken in drying the material employed.

Opianic Ether.—According to Wöhler, opianic ether cannot be obtained by the action of sulphuric or hydrochloric acid upon a mixture of opianic acid and alcohol ; but I obtained it by chance, with the latter acid, and have confirmed its composition and found it to possess the properties attributed to it by the discoverer.

Hemipinic Acid.—The analytical results obtained by Wöhler for this acid I have fully confirmed, but I have found it to be a bibasic acid, and its rational formula to be $C_{20} H_{10} O_{12}$, or double of that given by him.   This result is deduced from the analysis of an acid hemipinate of potass, and from the formation of a hemipinovinic acid.

Acid Hemipinate of Potash is obtained in the form of thick, six-sided tables, sometimes of considerable size, which are readily soluble in water and alcohol, but not in ether.   It is highly acid to test-paper.   The crystallised salt is represented by the formula :

$$KO . HO . C_{20} H_8 O_{10} + 5HO.$$
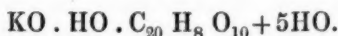
Neutral Hemipinate of Potash is highly soluble and crystallises with difficulty.

Hemipinovinic Acid is prepared by passing a current of hydrochloric acid through a solution of hemipinic acid in absolute alcohol. It is obtained in the form of tufts of bulky needles, sparingly soluble in cold, more so in hot water. It fuses at 270° Fahr., but melts under water into a transparent fluid. It is strongly acid to test-paper.   Its aqueous solution does not precipitate the salts of lead and silver, but gives, with perchloride of iron, a bulky, pale, brownish-yellow precipitate.   It dissolves readily in potash, and the solution, on boiling, evolves alcohol. The crystallised acid has the formula, $C_4 H_5 O . HO.$ $C_{20} H_8 O_{10} + HO$.   Although it possesses distinctly acid properties, and is capable of uniting with bases, I have failed in obtaining its compounds in a state of purity.   Its baryta-salt was obtained in tufts

of minute needles by digesting a solution of the acid with carbonate of baryta. But the compound was not obtained in a state fitted for analysis, and appears to be very liable to undergo decomposition.

ACTION OF NITRIC ACID ON COTARNINE.

The products of the action of nitric acid on cotarnine are extremely complex, and several different actions appear to occur simultaneously, in each of which a different decomposition is produced. When the concentrated acid is employed, oxalic acid is produced ; but when it is more dilute, another acid is obtained, which remains in solution in the nitric acid.

The preparation of this substance is a matter of considerable nicety, and it is particularly important that the nitric acid be not employed in too large an excess, partly on account of the risk of carrying the action too far, and partly on account of the difficulty of separating the product from a very large excess of acid. As the new product is liable to undergo a further oxidation, with production of oxalic acid, it is not safe to attempt its separation by evaporating the nitric acid solution. The best method is to dissolve the cotarnine in nitric acid diluted with about twice its bulk of water, and then adding strong nitric acid, to raise the mixture to the boiling-point. Red fumes are copiously evolved, and after some time, a little of the fluid is taken out and mixed with a considerable quantity of alcohol and ether. If, on standing for a short time, crystals are deposited, the whole fluid is treated in the same manner; but if they do not appear, the digestion is continued somewhat longer, and it is tried again, and so on, until the right point is attained. The fluid, mixed with alcohol and ether, is allowed to stand for twenty-four hours, and the precipitated crystals are separated by filtration. This substance agrees in all respects with the apophyllic acid obtained by Wöhler as a product of the action of bichloride of platinum upon cotarnine, but which he obtained in too small a quantity for examination and analysis.

Apophyllic Acid.—The acid, after being purified by crystallisation, and, if necessary, by animal charcoal, presents all the characters attributed to it by Wöhler, and may be obtained either in hydrated or anhydrous crystals. It is soluble in water, but not in alcohol or ether. It dissolves, also, in concentrated sulphuric acid. It fuses at 401° F., and on cooling solidifies into a crystalline mass. All its salts are extremely soluble. Its analysis gave results corresponding with the formula

$$C_{16} H_7 N O_8,$$
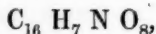
which has been confirmed by the analysis of its silver-salt. Its formation from cotarnine cannot be distinctly traced, as several other substances are formed simultaneously, which I have not examined;

but if we add to cotarnine two equivalents of oxygen and subtract from it the formula of apophyllic acid, the difference is $C_{10} H_6$:

$$
\begin{array}{lll}
\text{Cotarnine} + 2O & \quad . \quad . & C_{26} H_{13} \ N \ O_8 \\
\text{Apophyllic acid} & \quad . \quad . & C_{16} H_7 \ N \ O_8 \\
\hline
& & C_{10} H_6
\end{array}
$$

I have been unable to ascertain whether this group of atoms passes into any particular form of combination, or whether it is entirely oxidised, which is possible. In its composition, apophyllic acid is curiously related to anthranilic acid, from which it differs by two equivalents of carbonic acid.

$$\underbrace{C_{16} H_7 \ N \ O_8}_{\text{Apophyllic acid.}} = \underbrace{C_{14} H_7 \ N \ O_4}_{\text{Anthranilic acid.}} + 2CO_2$$
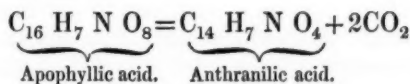
According to Wöhler, apophyllic acid, when distilled, yields a quantity of *Chinoline*; but now that its constitution is known, we should rather expect the production of aniline, which would be formed from it by the removal of four equivalents of carbonic acid, thus:

$$C_{16} H_7 \ NO_8 - 4 \ CO_2 = C_{12} H_7 \ N$$
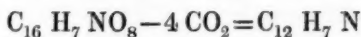
By distillation I obtained a quantity of a base which had a slightly aromatic odour, but gave no reaction of aniline with chloride of lime. I did not obtain it in sufficient quantity for analysis. It is not the only product of decomposition, a non-basic oil making its appearance at the same time.

Apophyllate of Silver.—This salt can only be obtained by digesting the acid with moist carbonate of silver, and precipitating with a mixture of alcohol and ether. It is thrown down as a crystalline powder, which is very soluble in water, and insoluble in alcohol and ether. It does not explode when heated, but burns slowly and leaves metallic silver. It is represented by the formula $AgO \ . \ C_{16} H_6 \ NO_7$.

Apophyllate and Nitrate of Silver.—When a solution of nitrate of silver is added to an alkaline apophyllate, a sparingly soluble crystalline salt is obtained, which explodes violently when heated, and has been described by Wöhler as apophyllate of silver. It is, however, a compound of that salt with the nitrate of silver, and is represented by the formula $AgO \ . \ C_{16} H_6 \ NO_7 + AgO \ . \ NO_5$.

Apophyllate of Ammonia forms very small prismatic needles, highly soluble in water.

Apophyllate of Baryta is obtained by digesting the acid with carbonate of baryta, and adding alcohol to the fluid, when it is precipitated in wart-like crystals.

Associated with apophyllic acid, another substance was once

obtained in yellow needles, the analysis of which gave results corresponding with the formula $C_{36} H_{13} NO_{14}$, but want of material has prevented its further examination, and on another occasion a third substance was detected. Both these substances deserve further examination.

When the solution from which the apophyllic acid has been thrown down is distilled, a syrupy fluid is obtained, which, on the addition of potash, evolves the odour of a volatile base. In order to obtain this base, a considerable excess of potash was added to the syrupy fluid, and the whole distilled. A highly alkaline fluid passed into the receiver, which was saturated with hydrochloric acid, evaporated, and the residue dissolved in absolute alcohol. The alcohol, on distillation, yielded a salt in fine scales, which gave a fine golden-yellow double salt with bichloride of platinum, and proved on analysis to be the platinum compound of methylamine. On another occasion the presence of ethylamine was detected; and indications of another base, with a much higher atomic weight, were also obtained.

The following is a tabular statement of the substances described in the paper.

Narceine	$C_{46} H_{29} NO_{18}$
Hydrochlorate of narceine .	$C_{46} H_{29} NO_{18} . HCl$
Platinochloride of narceine .	$C_{46} H_{29} NO_{18} . HCl . Pt Cl_2$
Robiquet's narceine .	$C_{32} H_{19} HO_{10}$ (?)
Thebaine . . .	$C_{38} H_{21} NO_6$
Hydrochlorate of thebaine .	$C_{38} H_{21} NO_6 . HCl + 2 HO$
Platinochloride of thebaine .	$C_{38} H_{21} NO_6 . HCl . Pt Cl_2 + 2 HO$
Teropiammon . . .	$C_{60} H_{29} NO_{26}$
Opianyl	$C_{20} H_{10} O_8$
Hydrate of opianyl . .	$C_{20} H_{10} O_8 + HO$
Opianic acid . . .	$C_{20} H_{10} O_{10}$
Opianic ether . . .	$C_4 H_5 O . C_{20} H_9 O_9$
Hemipinic acid . . .	$C_{20} H_{10} O_{12}$
Acid hemipinate of potash .	$KO . HO . C_{20} H_8 O_{10}$
Hemipinate of silver . .	$2 Ag O . C_{20} H_8 O_{10}$
Hemipinovinic acid . .	$HO . C_4 H_5 O . C_{20} H_8 O_{10}$
Apophyllic acid . .	$C_{16} H_7 NO_8$
Apophyllate of silver . .	$AgO . C_{16} H_6 NO_7$
Methylamine . . .	$C_2 H_5 N$
Ethylamine . . .	$C_4 H_7 N$

On the extraction of Oxygen Gas from Atmospheric Air.[*]

By M. Boussingault.

It is somewhat remarkable that no attempt has ever been made to obtain oxygen from the atmosphere in quantity sufficient for any useful purpose. In fact, the celebrated experiment of Lavoisier, in which he converted mercury into the red oxide, by boiling it for a long time in the air and afterwards decomposing the resulting oxide at a red heat, appears to be the only instance in which the oxygen of the air has actually been separated from the nitrogen, and exhibited in the free state; and it is scarcely necessary to observe, that the quantity yielded by this process, is insufficient for any purpose beyond the mere demonstration of the fact.

Among the very few substances which might be made available for the actual separation of oxygen from the air, baryta appears to present the greatest advantages, from its well known property of absorbing oxygen readily from the air at a low red heat, and passing to the state of peroxide of barium, which, on subsequent exposure to a full cherry-red heat, gives up its second atom of oxygen, and is reconverted into baryta. The baryta may thus be reoxidised at a low red heat, once more restored to its original state at a higher temperature, and thus the process may be made continuous.

The apparatus used for carrying this process into effect, consists of a tube of porcelain, or glazed earthenware, inserted through a dome-furnace. The baryta is introduced in fragments into this tube, at the entrance to which is placed a stopcock to regulate the access of air. To the other end of the tube are adapted two exit-tubes, also furnished with stopcocks; the one communicating with an aspirator, the other with a gasometer.

The tube is first raised to a dull red heat, and the air made to pass through it, by allowing the water to run from the aspirator; the baryta then becomes oxidised. After a certain time, when the oxidation is thought to be sufficiently advanced (it need not be complete), the stopcock which admits the air, and likewise the stop-cock of the aspirator are closed, and communication is established between the tube and the gasometer. The temperature is then raised by opening the ash-door of the furnace, and after a short time, the oxygen which the baryta had absorbed is given off, and passes into the gasometer. When the disengagement of gas is finished (and it is very rapid), the gasometer is closed, the fire lowered by closing the ash-door, and the aspirator again set in action. By this means the baryta is reoxidised, and will then give up a fresh portion of oxygen on being more strongly heated; and these two operations may be continually repeated. The baryta, in fact, at a red heat, acts

as a filter, which retains the oxygen of the air and lets the nitrogen pass.

In the course of the experiments made with this apparatus, it was found that the baryta, after having been used several times, and occasionally even after the second operation, lost, in a great measure, its power of absorbing oxygen.   This diminution of absorbing power was equally apparent when the baryta was oxidised in a current of air carefully freed from water and carbonic acid, and even when the oxidation was effected by a stream of pure oxygen; hence it was not due to any change produced in the baryta by carbonic acid, water, or other impurities in the air.   It was for some time attributed to a partial fusion or vitrification taking place at the surface of the baryta, in consequence of the presence of silica and alumina derived from the earthen vessels in which the baryta was calcined.   More careful experiments, however, showed that, with perfectly pure baryta, calcined in platinum vessels, the same diminution of absorbing power was apparent.

The true cause of the diminution was ultimately found in the gradual, but complete desiccation which the baryta undergoes by the continued passage of dry air over it.   In fact, M. Boussingault's experiments show that pure anhydrous baryta has very little tendency to absorb oxygen; but that the hydrate, when heated to dull redness in a current of air, readily gives up its water, and is converted into peroxide of barium.

Now, baryta prepared in the ordinary way is never perfectly dry; for though in calcining the nitrate, any water that may be present is driven off by the heat, the baryta nevertheless absorbs more or less water as it cools—more especially as, in order to remove it from the crucible, it is necessary to break it up.   Now, this partially hydrated baryta, when first subjected to the action of the air at a low red heat, absorbs oxygen with facility; but as its water is gradually abstracted, its power of absorption becomes less and less.

The easy conversion of hydrate of baryta into peroxide of barium by a current of dry air, joined with the well-known fact, that the peroxide is readily converted into the hydrate by boiling water or its vapour, suggests the means of separating the oxygen of the air at a much lower temperature than by the process already described, thereby economising fuel, and avoiding the destructive action which the baryta exerts upon the earthenware tubes at high temperatures. In fact, the decomposition of the hydrate, and oxidation of the baryta, take place at a dull red heat; and the decomposition of the peroxide by vapour of water may be effected at a still lower temperature, viz., at 100° C.

In carrying out this process, however, considerable difficulty was experienced from the extreme fusibility of the hydrate. This substance becomes liquid at a red heat; hence it was necessary to place it in a long silver boat, occupying the whole length of the heated portion

of the porcelain tube; but in a short time, the crust of peroxide
formed on the surface, opposed so great an obstacle to the action of
the air, that the oxidation took place very slowly. This inconvenience
was ultimately remedied by mixing the hydrate of baryta with hydrate
of lime, or with magnesia.

The mixture is introduced into a porcelain tube, and kept in its
place by two plugs of asbestos. It is then oxidised by a rapid
current of air, the tube being kept at a dull red heat; and when the
oxidation has proceeded far enough, the connexion with the gasometer
is established, and a jet of steam introduced into the tube from a
small boiler disposed for the purpose. The peroxide of barium is
then immediately reconverted into hydrate of baryta, and the excess
of oxygen is given off. The baryta is then reoxidised by a fresh
current of air, again deoxidised by vapour of water, and thus the
process is made continuous.

Baryta thus treated appears to retain its power of absorbing
oxygen for any length of time.

In the process just described, we have perhaps an example of the
influence of mass in chemical decomposition. In the one case, a
large quantity of air expels the water from hydrate of baryta, and
puts oxygen in its place; in the other, at the same temperature, a
continuous current of vapour of water expels the oxygen from
peroxide of barium, and reconverts it into hydrate of baryta.

This mode of extracting oxygen from the air has hitherto been
used only in laboratory experiments; but there appears to be no
reason against its use on the large scale. In fact, 10 kilogrammes of
baryta, if completely oxidised and deoxidised, will yield 730 litres of
oxygen gas; and even supposing that, for the sake of quickness of
operation, this quantity were reduced to 600, we might, by operating
on 100 kilogrammes of substance heated in eight or ten cylinders,
obtain at each deoxidation, 6000 litres of oxygen; and supposing
four or five such operations to be gone through in four-and-twenty
hours, the product would be from 24,000 to 30,000 litres of gas (or,
in English measures, from 5000 to 6000 gallons of gas from 8 or
9 cwt. of baryta).

As baryta is now prepared in large quantities, its use would not
present any difficulty; but in order that the process may be advan-
tageously conducted on the manufacturing scale, there are still many
points to be determined. Thus it would be necessary to determine
the manner in which the oxidation is affected by the velocity of the
current of air, and whether it would not be advisable to use hot air
in order to accelerate the operation, and avoid loss of heat. The
necessity for the presence of water in the oxidising process may be
considered as established; but it still remains to determine the
quantity of vapour which the air should contain, in order to act to the
greatest advantage.

Electro-Chemical Researches on the Properties of Electrified Bodies. *

By E. Fremy and E. Becquerel.

For some years, the attention of chemists has been directed to the singular modifications which certain bodies present when submitted to the action of a moderately elevated temperature.   It is known, for example, that sulphur and phosphorus, when thus treated, acquire new properties.   The authors propose to examine, in a series of memoirs, whether electricity is capable of altering the physical and chemical characters of bodies in a similar manner to heat; and have, in the first place, directed their attention to the remarkable effects presented by oxygen under certain circumstances, and commonly attributed to the formation of a peculiar principle, called *Ozone*. This body appears, in fact, to be produced whenever oxygen is subjected to electrical influence ; but its production, or the effects attributed to it, take place in different degrees according to the kind of electricity employed.

1. The voltaic battery cannot be used for determining the nature of ozone, because the amount of the active principle existing in the oxygen thereby obtained is very small.

2. The arc formed on breaking the voltaic current, does not appear to modify oxygen in the same manner as the ordinary spark, probably because the rise of temperature which accompanies it, destroys what the electricity might produce.   It appears, however, that the voltaic arc is capable of inducing the combination of gases, acting, in fact, like spongy platinum, or the common electric spark. The authors have, by means of the voltaic arc, induced the direct combination of nitrogen with oxygen, to form nitric acid ; of hydrogen with nitrogen, to form ammonia ; and of sulphurous acid with oxygen, to form anhydrous sulphuric acid.

3. The spark proceeding from induced currents, and produced by means of the apparatus lately constructed by M. Ruhmkorf, acts like the spark of the ordinary electrical machine, and enables the operator to repeat, without fatigue, all the experiments which can be made with the machine.

4. Pure oxygen enclosed in glass tubes, together with a strip of paper saturated with starch and iodide of potassium, may be electrified by induction, by means of a succession of sparks passing along the external surface of the tube ; the paper begins to turn blue after the passage of a few sparks.   This colouring is due to the electrization of the oxygen, and not to any electrolytic decomposition of the iodide ; for when the experiment is made in an atmosphere of hydrogen, no blueing is produced.   This fact is the more remarkable, inasmuch as

* Ann. Ch. Phys. [3], XXXV, 62 ; *abstr.* Compt. Rend. XXXIV, 399 ; J. Pharm. [3], XXXI, 321.

the oxygen is electrified without the intervention of metallic wires, and consequently when there can be no transference of particles by the spark.

5. Oxygen prepared by the most various methods, *e. g.*, by calcining the oxides of manganese, mercury, and silver, by the decomposition of chlorate of potash, and by the electrolysis of water, acquires a peculiar odour and very decided oxidating powers when subjected to the influence of electricity; these properties are exhibited by oxygen in the greatest state of purity obtainable. Oxygen thus electrified, loses its oxidating properties when placed in contact with iodide of potassium; but its odour and oxidizing powers may be restored by fresh electrization; this experiment may be repeated any number of times with the same gas.

These facts show that the oxidating power of electrified oxygen is not due to the presence of any foreign substance in the gas. The following experiments were made for the purpose of rendering a given volume of oxygen totally absorbable in the cold by mercury, silver, or iodine of potassium.

6. When pure, dry oxygen gas is enclosed in a series of glass tubes, and submitted, as above, to the action of the electric spark, and one end of each tube then broken, to find how much of the gas has been rendered capable of absorption by the alkaline iodide, it is found that for several hours the modification increases in proportion to the time of electrization, and afterwards appears to diminish, probably because the spark destroys that which it had before produced.

7. The difficulties attending the preceding experiment, induced the authors to study the action of electrized oxygen on certain absorbing substances, capable of immediately taking up the oxygen which has been subjected to the action of electricity, and thereby removing it from the decomposing action of an excess of that agent. A series of electric sparks was therefore passed through small eudiometric tubes filled with oxygen, and either placed over moist mercury or a solution of iodine of potassium, or having a moist silver plate introduced into them. The oxygen was then regularly absorbed under the influence of the electric spark, and in several experiments, complete absorption took place.

8. Finally, to remove all doubts respecting the particular activity imparted to oxygen by the electric spark, the preceding experiments were repeated with sealed tubes. For this purpose, iodide of potassium and moist silver were introduced into tubes filled with pure oxygen, and the tubes were then sealed. These tubes were subjected for several days to electric action; the spark, which was very brilliant at first, became paler and paler; and, after a while nearly invisible. The ends of the tubes were then broken under water, whereupon the water rushed in and filled them com-

pletely, showing that the oxygen had been entirely absorbed in the cold by the silver and by the alkaline iodide. To render these experiments decisive, it was previously ascertained: I. That the oxygen is not absorbed by pure water, by the sides of the glass vessel, or by the platinum wires; II. That the presence of water is required, not to develop the activity of the oxygen, but to enable the active oxygen to act on the metals and the alkaline iodide; III. That the electric spark does not decompose iodide of potassium by influence.

The experiments above described may be considered as affording rigorous proof that oxygen may, by the influence of electricity, be rendered wholly absorbable at ordinary temperatures, by iodide of potassium, and by several metals—mercury and silver, for example. They likewise confirm the latest results obtained by Schönbein, Marignac, and De la Rive, respecting the nature of the so-called *ozone*, and show that electricity by acting upon oxygen, develops new properties, which did not exist in it before. The authors therefore propose to give the name of *Electrized Oxygen* to the gas thus modified by electric influence, and to abandon the term *Ozone*, which gives the idea of the transformation of the oxygen into another body.

On the preparation of pure Acetic Acid from Wood-Vinegar and Brandy-Vinegar.[*]

By C. Volckel.

The ordinary mode of preparing pure acetic acid from wood-vinegar, viz., by converting the latter into acetate of soda, freeing this salt from empyreumatic substances by roasting and fusion, and then decomposing it by sulphuric acid, is both tedious and expensive, in consequence of the roasting and repeated crystallizations required; consequently, the acetic acid thus obtained cannot be economically used for the preparation of pure acetate of lead, that salt being in fact obtained much more cheaply from brandy-vinegar. Various attempts have therefore been made to purify the acetic acid in wood-vinegar at a cheaper rate; and for this purpose the author proposes the following process, consisting essentially in the conversion of the crude acid into acetate of lime, and the decomposition of that salt by hydrochloric acid.

To obtain acetate of lime in a sufficient state of purity, the crude acid is saturated with lime, without previous distillation, whereupon a part of the resinous impurities separate out in combination with lime, while the rest remain in the liquid, imparting to it a dark

brown colour; and the liquid is clarified by filtration, or by simply leaving the impurities to settle down, and afterwards evaporated in an iron pot to about one half its bulk. Hydrochloric acid is then added in such quantity, that a small sample of this liquid may distinctly redden litmus after cooling. This causes the dissolved resin to separate and collect together in the boiling liquid, so that it can easily be skimmed off—and likewise decomposes the lime-compounds of creosote and other volatile substances, which may then be expelled by further evaporation. The quantity of hydrochloric acid required for this purpose, varies of course with the constitution of the wood-vinegar, which again varies with the degree of moisture of the wood from which the acid is obtained; but the average quantity is from 4 to 6 pounds for 150 litres (33 gallons) of the wood-vinegar. The solution of acetate of lime is then further evaporated, and ultimately dried at a high temperature, to drive off all volatile substances. The evaporation and drying may generally be performed in the same iron vessel; but in operating on a very large scale, it is best to dry the salt on cast-iron plates: the drying requires the greatest care. The volatile empyreumatic substances adhere very tenaciously to the acetate of lime, and to the resin contained in it, and unless driven off by heat, they pass over in the subsequent distillation together with the acetic acid, and impart to it a bad odour. The drying must therefore be continued till the acetate of lime becomes inodorous, or nearly so. When thoroughly dried, it has a dirty-brown colour.

To obtain the acetic acid from this salt, it is distilled with hydrochloric acid. The distillation may be performed in a still, with copper head and leaden condensing-tube; if the operation be conducted with proper care, neither copper nor lead is found in the distillate. The quantity of hydrochloric acid required cannot be exactly given, because the acetate of lime contains variable quantities of foreign matters, viz., resin, and chloride of calcium already formed. In general, however, from 90 to 95 parts of hydrochloric acid, of 20° Baumé, or sp. gr. 1·16, will completely decompose 100 parts of acetate of lime, without causing the distillate to be much contaminated with hydrochloric acid. In any given case, the quantity of hydrochloric acid required is easily determined by an experiment on a small scale. The apparatus may likewise be so arranged, as to allow of the subsequent addition of hydrochloric acid, in case of the quantity first put in being found insufficient. Whether the quantity introduced is sufficient, may be known by testing the distillate with nitrate of silver; so long as mere turbidity is produced, we may be sure that the hydrochloric acid is not in excess.

The distillation of the acetic acid proceeds with ease and regularity. The acetate of lime dissolves in the hydrochloric acid, forming a dark-coloured liquid, while a quantity of coloured resin separates out. As the whole mass is liquid, the heat diffuses through it easily; and

as the acetic acid passes over between 100° and 120°, and the acetate of lime has been already exposed in drying to a higher temperature, the distilled acid is but very slightly contaminated with empyreumatic products resulting from decomposition of the resin. Moreover, the resinous matters, being lighter than the chloride of calcium solution, float on the top, and do not form hard incrustations in the still.

The distilled acetic acid has but a very slight empyreumatic odour, which is also very different from that of crude wood-vinegar. It is perfectly colourless, and, if the hydrochloric acid has not been added in excess, gives but a slight cloud with nitrate of silver. Any yellow tint that it may exhibit, arises from particles of resin mechanically carried over; for the resin separated from the acetate of lime by the hydrochloric acid, melts as the temperature rises, and forms a fluid layer on the surface of the chloride of calcium solution, which is very apt to cause spirting. The resin should therefore be moved as far as possible before distillation, either by skimming it off with a spoon, or by filtering through a linen cloth.

The specific gravity of the acetic acid obtained by this process, varies from 1·058 to 1·061, corresponding nearly to 8° Baumé, or 10° Beck. It contains more than 40 per cent of anhydrous acetic acid.

As, however, acetic acid of this degree of concentration is rarely used, and a somewhat weaker acid is more easily separated by distillation from the solution of chloride of calcium, it is better to add a certain quantity of water, either before or towards the end of the distillation. A good proportion is :—100 parts acetate of lime, from 90 to 95 of hydrochloric acid, and 25 of water. This gives from 95 to 100 parts of acetic acid, of 7° Baumé, or sp. gr. 1·105. In this manner 150 litres of wood-vinegar will yield 60 pounds of acetic acid of this strength.

The acetic acid thus obtained, may be still further purified by mixing it with a small quantity of carbonate of soda, and distilling it again. The acid which passes over is free from hydrochloric acid and perfectly colourless, but still retains a slight empyreumatic odour. But even this may be removed by distilling it with 2 or 3 per cent of bichromate of potash instead of carbonate of soda.

Acetic acid purified with bichromate of potash is, in fact, undistinguishable from that which is obtained from pure acetate of soda by distillation with sulphuric acid, or from pure acetate of lime with hydrochloric acid. It does not exhibit the slightest colour when heated with strong sulphuric acid, nor does it reduce the smallest quantity of silver when boiled with nitrate of silver and ammonia. When saturated with oxide of lead, it also yields a colourless salt, the analysis of which agrees perfectly with that of pure acetate of lead. Peroxide of manganese may also be used for the purification, instead of bichromate of potash; but the acid thus purified, gives, after a while, a slight turbidity with nitrate of silver; any empyreu-

matic odour that it may retain may be removed by digestion with purified animal charcoal.

As the acetic acid can be so easily freed from hydrochloric acid, a slight excess of the latter during distillation is not injurious; on the contrary, the presence of a small quantity of hydrochloric acid is very useful for the purification of the acetic acid with manganese or bichromate of potash.

The rectification of acetic acid with bichromate of potash or with manganese, may be very well conducted in a copper still, with leaden condensing tube: the acid thus prepared can only be contaminated with a small quantity of acetate of lead. If, however, access of air be prevented* during the distillation, this impurity will be confined to the first and last portions of the distillate; and by collecting these apart, to be used for the preparation of acetate of lead, the greater part of the acid may be obtained free from lead. With these precautions, the use of glass or silver heads and condensing tubes may be dispensed with.

The preparation of acetic acid by the method just described, may be rendered simpler by subjecting the wood-vinegar to a previous distillation, and thereby removing the greater part of the resin. But this previous distillation entails increased expense for labour and fuel, because the same liquid must be twice evaporated; moreover, part of the acetic acid remains with the tar in the still. On the small scale the loss thus occasioned is unimportant; but in a large manufactory, it would amount to something considerable in the course of a year.

The expense occasioned by previous distillation of the wood-vinegar may be avoided by the use of a compound still. The vapour of the wood-vinegar, instead of being condensed immediately, is made to pass into a copper receiver containing the quantity of lime required to saturate the acid, which is thereby completely absorbed. If the copper receiver be surrounded by some substance which is a slow conductor of heat, but little aqueous vapour condenses in it. This vapour may be advantageously used to evaporate a solution of lime resulting from a previous operation. This process is, however, more complicated, and does not yield more acetic acid than the simpler one first described.

The method here recommended is much cheaper, and yields a much purer product than the ordinary method of distilling impure acetate of lime with sulphuric acid. Moreover, by the addition of hydrochloric acid during the evaporation of the impure acetate, the volatile, slightly acid bodies contained in the wood-vinegar, are removed much more easily than by the use of a solution of chloride of calcium (Schnedermann), or by roasting the impure acetate of

* The entrance of air into the condensing-tube may be prevented by closing the end of the tube with a cork, through which is inserted a glass tube, bent in the form of an S.

lime, either alone or with hydrate of lime (Kestner, Schwarz). In the latter process, even if it attains the desired end, a considerable loss is incurred from decomposition of the acetate of lime, inasmuch as that substance, from its infusibility, does not admit of any exact regulation of the heat.

The use of hydrochloric instead of sulphuric acid, in the decomposition of the acetate of lime, has this great advantage, that the presence of resins, colouring matter, &c., in the acetate of lime, does no harm, provided the acetate has been sufficiently heated to drive off these free volatile substances. When, on the contrary, sulphuric acid is used, the acetic acid produced always has a bad odour, is saturated with sulphurous acid, and contaminated by various products arising from the decomposition of the resins at an elevated temperature. Moreover, the sulphate of lime forms a hard crust at the bottom of the still, and in distilling on the large scale, the bottom of the still must be heated red-hot to drive out all the acetic acid. The last portions of acid that pass over are often turbid from the presence of separated sulphur; and the odour of sulphuretted hydrogen becomes perceptible, that substance arising from reduction of the sulphate of lime to sulphide of calcium at the bottom of the vessel: from this cause, cast-iron stills soon become corroded.

The low price at which pure acetic acid may be obtained by the method above described, will probably lead to a more extended use of it in dyeing and calico printing. The acid thus obtained may, likewise be advantageously used in the preparation of acetates, especially of acetate of lead.

Pure Acetic Acid from Brandy-Vinegar. A similar process may be adopted for the preparation of pure acetic acid from brandy-vinegar; the process, however, is simpler, inasmuch as brandy-vinegar is much less impure than wood-vinegar.

Strong brandy-vinegar (the best for this purpose is that which contains from 12 to 15 parts of anhydrous acetic acid—a proportion which is obtained in some manufactories by a process at present not much known) is saturated with lime; and the turbid and coloured solution is strained through a linen cloth, and evaporated to dryness in an iron vessel. The dried salt is perfectly white, the colouring matters previously contained in the solution having been for the most part destroyed by the oxidizing action of the air.

The decomposition of the acetate of lime is effected by hydrochloric acid in the manner already described, excepting that, the acetate of lime being less mixed with foreign matter than that obtained from wood-vinegar, a larger proportion of hydrochloric acid is required for its decomposition, viz., about 130 parts of acid to 100 parts of the lime-salt.

The final purification of the acid may be effected by either of the methods above described.

On Œnanthic Ether and Œnanthic Acid.[*]

By W. Delffs.

Œnanthic ether was first investigated in 1836 by Liebig and Pelouze,[†] who assigned to it the formula

$$C^{18} \; H^{18} \; O^3 = C^4 \; H^5 \; O \; . \; C^{14} \; H^{13} \; O^2$$

relying, in the calculation of their analyses, chiefly on the vapour-density; this they found to be 10·508, a result agreeing very closely with calculation, assuming that the vapour was condensed to *two* volumes. At present, however, organic compounds in general, and the ethers more especially, are regarded as condensed to 4 volumes, so that œnanthic ether, considered as above, presents an anomaly which throws some doubt on the correctness of the calculation, more especially as compounds of purely organic origin rarely have so high a vapour-density as that just quoted. Moreover, the formula $C^{14} \; H^{13} \; O^2$ can scarcely be the correct expression of the composition of anhydrous œnanthic acid; first, because it would require us to suppose that in the lead and silver-salts, 3 atoms of acid are united with 2 atoms of base, which is very unusual in organic acids; and secondly, because the occurrence of an acid with only 2 atoms of oxygen is scarcely to be found in the whole range of organic chemistry, certainly not among the *fatty* acids. Lastly, the relation between the composition and boiling points of organic compounds shows that the composition of œnanthic ether must be different from that which is given by Liebig and Pelouze. These considerations induced the author to submit this body to a further examination, which led to the following results.

1. *Œnanthic Ether.*—The substance employed had a yellowish colour, and feebly acid reaction. When subjected to fractional distillation, it began to boil at 240° C. The temperature then rose steadily to 246°, where it began to be stationary. The receiver was then changed, and the distillation continued for two hours, during which time the thermometer did not rise above 250°. The liquid which passed over during this interval, amounting to nearly the fourth part of the crude ether, was used in the following experiments. It was perfectly colourless, but still slightly acid; it was therefore washed with solution of carbonate of soda, dried by chloride of calcium, and rectified.

When the ether thus purified was used for the determination of the boiling-point, it again acquired a yellowish tinge; and when boiled over a spirit-lamp, either with or without platinum wire, exhibited a very peculiar phenomenon, bubbles of vapour bursting from the

liquid from time to time, with a noise as if the retort were cracking, and giving rise each time to a visible cloud of condensed vapour. This phenomenon was not exhibited when the ether was heated on a sand-bath. It differed from the well-known sudden agitation which many liquids present in boiling, by not causing any perceptible interruption to the quiet progress of the ebullition. After the ether had been rectified a second time, when a yellowish residue again remained, this effect was but very slightly exhibited, though the boiling-point differed from the former by scarcely half a degree.

The ether thus purified was colourless, had a pleasant vinous odour, and a taste, slight at first, but afterwards irritating to the throat, Sp. gr. = 0·8725 at 15·5° C. Index of refraction = 1·414 at 13·5° C. Boiling-point very constant at 224°, under a pressure of 27″ 8‴·1, with the mercury at a temperature of 14°.

The analysis of the ether with oxide of copper gave, carbon 70·5 and 70·6 per cent; hydrogen 11·8, numbers agreeing very closely with the formula $C^{22} H^{22} O^4$. The vapour-density was found by experiment to be 7·042; calculation from the formula, $C^{22} H^{22} O^4$, gives 6·449. The difference is somewhat greater than is desirable, but is sufficiently accounted for by the impossibility of heating the vapour to the necessary temperature above the boiling-point without decomposing it.

Œnanthic Acid.—Œnanthic ether is rapidly decomposed by heating it with caustic potash; and on subsequently adding hydrochloric acid to the solution, œnanthic acid separates in the form of a slightly yellowish oil, which solidifies on cooling, in a snow-white mass, showing scarcely any traces of crystallization. It is readily dissolved by alcohol, even in the cold, and in almost every proportion by ether; from the alcoholic solution it separates by spontaneous evaporation as a crystalline mass. When pure, it is perfectly destitute of taste and smell, and melts even with the heat of the hand. The accurate determination of the melting-point is difficult, as the acid passes into a buttery state before melting, but it is certainly below 25° C. The acid dissolves easily in ammonia, forming a solution which dries up, even on spontaneous evaporation, to a greasy soap, which does not again form a clear solution in water. The solution of the ammoniacal salt, made as neutral as possible, formed, with nitrate of silver, a white curdy precipitate, which did not dissolve perceptibly in boiling water. This salt, when thoroughly washed and dried, gave, on analysis, numbers corresponding with the formula:

$$AgO . C_{18} H_{17} O_3 \text{ or } C_{18} \begin{matrix} H_{17} \\ Ag \end{matrix} O_4$$
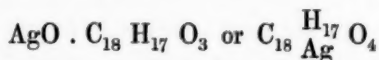
The composition of the hydrated acid must therefore be $C_{18} H_{18} O_4$, a formula with which the analysis made by Liebig and Pelouze agrees

sufficiently well, when their results are calculated according to the atomic weight of carbon at present adopted.

From this it appears than œnanthic acid is identical in composition with pelargonic acid as analyzed by Redtenbacher and Pless.* The two acids appear also to be similar in properties, so far, at least, as Redtenbacher has determined those of pelargonic acid. The identity in composition was likewise confirmed by the analysis of the baryta-salt of œnanthic acid. Pelargonate of baryta is said by Redtenbacher to resemble the crystals of cholesterin. Such a resemblance was not observed in the œnanthate; but its absence is of little importance, as the author has, on other occasions, observed considerable differences in the appearance of crystals of butyrate of baryta, though they are always, as Lerch† states, perfectly anhydrous.

There is one point in Liebig and Pelouze's investigation which must for the present be left undecided, viz., the change which œnanthic acid undergoes by distillation. This the author was unable to investigate properly, for want of material; but the portions which passed over at a high temperature appeared to contain an acid having a higher equivalent (capric acid ?).

In a note appended to this paper, the author states that the conversion of organic baryta-salts into carbonate of baryta by ignition in a flat platinum dish, affords a very convenient mode of ascertaining the atomic weight of an organic acid.

On Sorbine, a new saccharine substance, extracted from the berries of the Mountain Ash.‡

By J. Pelouze.

The berries of the mountain ash contain, amongst other substances, malic acid, malate of lime, and grape-sugar; their great acidity forbids the supposition that they contain ordinary cane-sugar; but Pelouze has succeeded in obtaining from them a sugar, differing in many essential properties from any of the sugars previously known.

The berries, gathered towards the end of September, were crushed and squeezed through linen. The juice thereby obtained was left to itself in earthen vessels for thirteen or fourteen months, during which time it yielded deposits and vegetations which were not examined. The liquid, which at length clarified spontaneously, was decanted, and then evaporated at a gentle heat to the consistence of a thick syrup. This syrup deposited a quantity of dark-brown

* Ann. Ch. Pharm. LIX, 52. † Ibid. XLIX, 216.
‡ Ann Ch. Phys. [3], XXXV, 223; J. Pharm. [3], XXI, 321.

crystals which were completely decolourized by treating them twice
with animal charcoal.   By successive concentration of the mother-
liquid, fresh quantities of crystals were obtained and purified in a
similar manner.

The crystals thus contained consist of a new substance, to which
the author gives the name of Sorbine.   By analysis they yielded
in 100 parts: carbon, 40·00: hydrogen, 6·66; oxygen, 53·34,
agreeing with the empirical formula CHO.   The numbers have been
confirmed by MM. Cahours and Cloez, to whom a specimen was
sent for analysis.

To determine the rational formula, a solution of acetate of lead,
slightly ammoniacal, was added to a solution of sorbine in excess ; a
white precipitate was then formed, which, when washed and dried,
yielded by analysis numbers which agreed nearly with the formula
$4 \, PbO \, . \, C_{12} \, H_9 \, O_9$.   Hence it would appear that the formula of
aqueous sorbine is :

$$C_{12} \, H_9 \, O_9 \; . \; 3 \, HO \; \text{or} \; C_{12} \, H_{12} \, O_{12}.$$

Sorbine combines with common salt, forming crystals which, when
examined by the microscope, appear to be cubic.

Sorbine is colourless, and has a pure sweet taste, which cannot be
distinguished from that of cane-sugar.   The crystals are perfectly
transparent, hard, and grate between the teeth like sugar-candy.
They are rectangular octohedrons, belonging to the right prismatic
system.   Their density at 15° is 1·654.   Water dissolves more than
twice its weight of them ; boiling alcohol, on the contrary, dissolves
but a very small quantity, which it deposits again on cooling,
in octohedral crystals, similar to those which are obtained from the
aqueous solution.

A concentrated solution of sorbine resembles the syrup of ordi-
nary sugar.   Its density, determined upon a liquid which was not
quite pure, was 1·372 at 15°.   Both sorbine itself, and the syrup
which it forms with water, are somewhat denser than cane-sugar and
its syrup.

Sorbine dissolved in water and mixed with yeast showed no signs
of fermentation, even after twenty-four hours' exposure to a tem-
perature of 20°—30° C.   Dilute sulphuric acid produces no change
in it, and does not render it fermentable.

Strong sulphuric acid attacks sorbine rapidly, first colouring it
reddish-yellow, and then, under the influence of a gentle heat,
changing it into a black carbonaceous substance, which the author
has not yet examined.   When nitric acid, either concentrated or
diluted with half its weight of water, is heated with sorbine, abundance
of red fumes are given off, and oxalic acid is produced, equal in weight
to more than half the sorbine used ; in fact the action is perfectly

similar to that which takes place with cane-sugar. The author has not yet determined whether any intermediate product is formed.

A solution of sorbine heated with alkalies acquires a deep yellow colour, and exhales an odour of caramel. Water containing $\frac{1}{2000}$ of sorbine becomes perceptibly yellow when heated with potash. Sorbine dissolves a considerable quantity of lime. The filtered liquid turns yellow when heated, depositing a flocculent precipitate, and giving off a distinct odour of caramel. Baryta acts in the same manner as lime. Oxide of lead also dissolves in a hot solution of sorbine, forming a yellow liquid, which has the odour of burnt sugar.

Sorbine yields no turbidity with subacetate of lead, but on the addition of ammonia, a white precipitate is formed.

Sorbine dissolves hydrated protoxide of copper, forming a deep blue solution, which gradually deposits a red precipitate of the suboxide. Tartrate of copper and potash is also reduced by sorbine, either hot or cold.

Sorbine, strongly heated on platinum-foil, or thrown upon a hot coal, behaves like common sugar, fusing, turning yellow, exhaling a strong odour of caramel, and leaving a bulky charcoal. But when it is carefully heated for some time to a temperature between 150° and 180° C., it gives off vapour of water slightly acid, and is converted into a new acid, which remains in the form of a deep-red body.

To obtain this acid pure, the residue is dissolved in potash or ammonia, the solution filtered, and supersaturated with dilute hydrochloric acid. The acid is then precipitated in deep-red flakes, which are washed with distilled water, and then dried in a stove at a temperature between 120° and 150°. The author distinguishes this new acid by the name of SORBIC ACID.

Sorbic acid is amorphous, of a very deep-red colour, insoluble in water, alcohol, and weak acids, but very soluble in potash, soda, and ammonia, with which it forms solutions having a very rich sepia colour. A mere trace of sorbic acid is sufficient to impart a sensible colour to an alkaline liquid.

The soluble salts of lime, baryta, alumina, iron, tin, gold, and platinum, form with soluble sorbates, bulky precipitates, exhibiting reddish-yellow colours of various degrees of intensity. Sulphate of copper yields a yellowish-green precipitate, soluble in excess of ammonia, to which it imparts a very deep-green colour.

Sorbic acid is found by analysis to contain: carbon, 57·96; hydrogen, 5·51; oxygen, 36·53; and the sorbate of lead consists of 51·35 oxide of lead with 48·65 sorbic acid. Hence if the formula of sorbic acid be $C^{32} H^{18} O^{15}$, that of the lead-salt will be $3PbO . C^{32} H^{18} O^{15}$.

Sorbine acts upon polarized light; when dissolved in water or in acids, it turns the plane of polarization *to the left*; in this respect

it differs from other crystallizable sugars, all of which turn the plane of polarization *to the right.*

On the Constitution of Citric Acid.[*]
By L. Pebal.

The author commences his paper with a sketch of the principal views which have been entertained respecting the constitution of citric acid, dwelling chiefly on those of Berzelius and Liebig. Berzelius[†] regarded citric acid as monobasic, assigning to the acid contained in the neutral citrates the composition, $C_4 H_2 O_4$. This view rested chiefly on an experiment, from which it appeared that the crystals obtained by cooling a solution of citric acid saturated at $100°$ C. had the composition $HO . C_4 H_2 O_4$, and did not give off any water when heated to $100°$. On the contrary, the crystals obtained from a solution saturated at ordinary temperatures, lost at $100°$ a quantity of water, which, if their composition were denoted by the formula, $HO . C_6 H_3 O_6 + Aq$.[‡] would amount to one equivalent; hence, the last-mentioned crystals, if referred to the atomic weight of citric acid first given, would contain, after dehydration, $\frac{1}{3}$ eq. of water less than the crystals obtained from the hot solution, likewise dried at $100°$.

Liebig,[§] on the contrary, regards the acid as terbasic, and expresses the several compounds just mentioned by the following formulæ:

$3 HO . C_{12} H_5 O_{11} + 2 Aq =$ acid crystallized from a solution saturated at ordinary temperatures.

$3 HO . C_{12} H_5 O_{11} + Aq =$ crystals obtained by Berzelius from a hot saturated solution.

$3 HO . C_{12} H_5 O_{11} = $ the first compound dried at $100°$ C.

The second formula is evidently equivalent in numbers to that of Berzelius, $HO . C_{12} H_2 O_4$. taken three times; if, however, it be correct, one-fourth of the water, that namely which is supposed to exist as water of crystallization, should go off at $100°$ C., whereas, according to Berzelius, it does not. Marchand,[||] however, found that the crystals obtained from a hot saturated solution, gave results agreeing with the formula $HO . C_4 H_2 O_4$, only when analyzed immediately after removal from the mother-liquor; but that when they were left for a while in vacuo over sulphuric acid, they gave off $2·2$ per cent of water without losing their transparency, and their composition then agreed exactly with that of ordinary citric acid, dried at $100°$, viz.,

* Ann. Ch. Pharm. LXXXII, 78.
† Pogg. Ann. XXVII, 281; Ann. Ch. Pharm. V, 129, 134, 137.
‡ Prout. Pogg. Ann. XII, 271.
§ Compt. rend. V, 863; Ann. Ch. Pharm. XXVI, 113.
|| J. pr. Chem. XXIII, 60.

3 HO . C_{12} H_5 O_{11}. The excess of water which the crystals contain on being first separated from the liquid can, therefore, only be regarded as adhering moisture. This result has been completely confirmed by the experiments of Pebal.

Liebig's view of the constitution of citric acid is likewise confirmed by the formula of citric ether as determined by Dumas,[*] viz: 3 Ae O . C_{12} H_5 O_{11}, and by those of the citrates of methyl, determined by Evre,[†] viz., 3 Me O . C_{12} H_5 O_{11}, and 2MeO . HO . C_{12} H_5 O_{11}.

The following experiments of Pebal, on the anilides of citric acid, likewise tend to establish the terbasic formula.

Crystallized citric acid in the state of powder, was mixed with a slight excess of aniline containing water (i.e., in the state in which it separates as an oily body under water) and heated in a glass flask to $140° - 150°$ C. till the emission of vapour-bubbles began to slacken. On cooling, it solidified to a brown-red glass, which was exhausted with boiling water; and the residue, which, meanwhile, had assumed the form of a pale yellow powder, was dried, dissolved in strong alcohol, and decolourized with animal charcoal.

The aqueous extract, after evaporation, deposited a small quantity of an acid crystalline mass consisting of citromonanilic acid, a substance to be hereafter described. The alcoholic solution yielded crystals of three different substances, two of which had the form of thin prisms, and the third that of hexagonal tables. Of the two kinds of prismatic crystals, the one became dull and opaque when left to stand over sulphuric acid covered by a bell-jar, while the others remained unaltered under the same circumstances. The largest portion of these crystals consisted of:

Citronanilide, C_{48} H_{23} N_3 O_8.—This substance is insoluble or very sparingly soluble in water; sparingly, also, in boiling alcohol, from which it crystallizes by spontaneous evaporation in flat, colourless, rectangularly truncated prisms, attaining the length of about 3 millimetres. They are sometimes very slender, generally arranged in concentric masses, longitudinally striated, and have a mother-of-pearl lustre. Their solution has no action on vegetable colours. Strong solution of potash or ammonia does not decompose the crystals, and may, therefore, be used to purify them from the six-sided tables, which are dissolved by the strong alkali. This substance may be regarded as terbasic citrate of aniline *minus* 6 HO.

$$\left. \begin{array}{l} C_{12}\ H_7\ N\ .\ HO \\ C_{12}\ H_7\ N\ .\ HO \\ C_{12}\ H_7\ N\ .\ HO \end{array} \right\} C_{12}\ H_5\ O_{11} - 6\ HO = C_{48}\ H_{23}\ N_3\ O_8$$
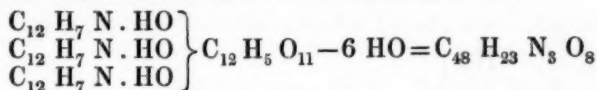
Citrobianil, C_{36} H_{16} N_2 O_8. — The six-sided laminæ already spoken of. Probably the best mode of preparing this compound by

* Compt. rend. VIII, 528.   * Ibid. XXI, 1441.

itself, would be to mix citric acid with aniline in the proportion required to form a bibasic salt, and heat the mixture to 150° C. as long as any perceptible evolution of hydrogen took place. The coloured crystals may be purified by treating their alcoholic solution with animal charcoal and recrystallizing. The solution of the pure substance, which does not alter the colour of litmus-paper, yields, by spontaneous evaporation, six-sided laminæ or tables of the diameter of about 5 millimetres. They are transparent, and dissolve very sparingly in water, but easily in boiling alcohol. By boiling with strong ammonia, they are converted into citrobianilic acid. The crystals, after drying in the air, do not lose weight by being kept over sulphuric acid.

Citrobianil may be supposed to be formed from bibasic citrate of aniline by separation of 6 HO:

$$\left. \begin{array}{l} C_{12}\ H_7\ N\ .\ HO \\ C_{12}\ H_7\ N\ .\ HO \\ \phantom{C_{12}\ H_7\ N\ .}HO \end{array} \right\} C_{12}\ H_5\ O_{11} - 6\ HO = C_{36}\ H_{16}\ N_2\ O_8.$$
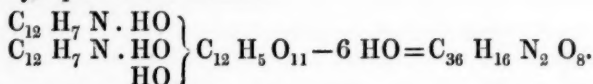
The four-sided, obliquely-truncated needles, which were obtained simultaneously with the citronanilide and citrobianil, and distinguished by the property of efflorescing when placed over sulphuric acid, lost at 100° about 1·08 per cent of their weight after drying in the air. They were found to contain 66·71 per cent carbon and 5·0 per cent. hydrogen, numbers which agree exactly with the composition of citrobianil; but the quantity obtained was not sufficient to enable the author to speak positively as to their identity.

Citrobianilic Acid, $C_{36}\ H_{18}\ N_2\ O_{10}$ or $HO\ .\ C_{36}\ H_{17}\ N_2\ O_9$.—When citrobianil is boiled with strong ammonia, it gradually dissolves, and is converted into the ammonia-salt of citrobianilic acid. The solution mixed with hydrochloric acid, deposits the acid in the form of a curdy precipitate, which is soluble in alcohol; and the alcoholic solution, which reddens litmus, yields the acid in soft silky needles radiating from several centres; they dissolve readily in alcohol, but sparingly in water. The acid melts at about 153°, giving off water and being converted into citrobianil. It may indeed be regarded as formed from citrobianil by taking up 2 eq. water:

$$C_{36}\ H_{16}\ N_2\ O_8 + 2HO = C_{36}\ H_{18}\ N_2\ O_{10},$$
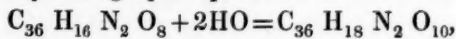
and its composition is that of bibasic citrate of aniline, *minus* 4 HO.

$$\left. \begin{array}{l} C_{12}\ H_7\ N\ HO \\ C_{12}\ H_7\ N\ HO \\ \phantom{C_{12}\ H_7\ N\ }HO \end{array} \right\} C_{12}\ H_5\ O_{11} - 4\ HO = C_{36}\ H_{18}\ N_2\ O_{10}.$$
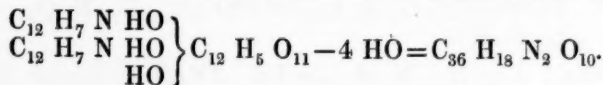
Citrobianilate of Silver, $AgO\ .\ C_{36}\ H_{17}\ N_2\ O_9$, was obtained by mixing a neutral solution of the acid in ammonia with nitrate of silver;

it formed a white precipitate. The *Baryta-salt*, Ba O, $C_{36} H_{17} N_2 O_9$, was obtained, in a similar manner, by double decomposition, in the form of a white, amorphous precipitate. The *Aniline-salt*, $C_{12} H_7 N . HO . C_{36} H_7 N_2 O_9$, was obtained by digesting the acid at a moderate heat with aqueous aniline. On evaporating the solution, the salt was deposited in colourless, transparent laminæ, which suffered very little diminution in weight by drying over sulphuric acid. The composition of these salts show that the acid is monobasic.

Monobasic Citrate of Aniline.—An alcoholic solution of citric acid was mixed with the proper quantity of aniline containing a little water, and the mixture left in vacuo over sulphuric acid till it dried up to a viscid, brown-red mass. After some time, crystals began to form in it, and ultimately filled the whole mass. The whole was then triturated with a small quantity of alcohol, the liquid pressed through linen, the solid residue dissolved in strong alcohol, and the solution left to evaporate over sulphuric acid. The salt was then obtained in fine needles united into geodes. They fuse at 100°, dissolve readily in alcohol, and still more readily in water. Sometimes, after the mother-liquor has been poured off, the fine needles form a kind of frothy mass. The composition of this salt may be expressed by the formula:

$$C_{12} H_7 N . HO \left.\begin{matrix} \\ HO \\ HO \end{matrix}\right\} C_{12} H_5 O_{11}$$
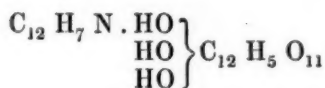
The two other aniline-salts show no tendency to crystallize.

Monobasic Citromonanilic Acid, $C_{24} H_{11} NO_{10}$.—When the salt just described is fused at a temperature of 140°—150°, water escapes, and the residual mass solidifies, partly while hot and partly on cooling, to a crystalline body, which dissolves very easily in water, provided an excess of aniline has been avoided, and separates by spontaneous evaporation, partly in crystalline globules, but more abundantly in the form of warty crusts consisting of small prisms. They may be rendered colourless by treatment with animal charcoal and recrystallization. They are likewise easily dissolved by alcohol; their solutions redden litmus-paper. The acid may be regarded as monobasic citrate of aniline *minus* 4 HO:

$$C_{12} H_7 N . HO \left.\begin{matrix} \\ HO \\ HO \end{matrix}\right\} C_{12} H_5 O_{11} - 4 HO = C_{24} H_{11} NO_{10}.$$
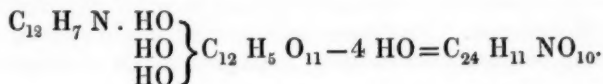
Silver-salt, AgO . $C_{24} H_{10} NO_9$.—An alcoholic solution of the acid neutralized with ammonia, gave a white precipitate with nitrate of silver. The liquid separated from this precipitate yielded, after a while, crystalline globules, which, when freed from a small quantity

of pulverulent matter adhering to them, were found to have the composition above given.

Aniline-salt, $C_{12} H_7 N . HO . C_{24} H_{10} NO_9$.—Formed by saturating the aqueous solution of the acid with aniline. Spherical geodes, easily soluble in alcohol.

Silver-salt of Bibasic Citromonanilic Acid.—The white precipitate obtained in the preparation of the silver-salt of the monobasic acid. Its composition is expressed by the formula :

$$2 Ag O . C_{24} H_{11} NO_{10}.$$
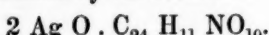
It was found impossible to obtain the hydrate of this acid, on account of its strong tendency to decompose. Its formula would be

$$2 HO . C_{24} H_{11} NO_{10} = C_{24} H_{13} NO_{12}.$$
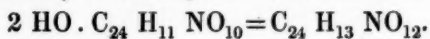
On the occurrence of Trimethylamine in Herring-brine.[*]

By Dr. Hofmann.

In the course of some observations on the ammonias of the methyl-series,[†] Dr. Hofmann has suggested that the base described by Wertheim under the name of *Œnylamine,* or *Propylamine,* may be identical with trimethylamine :

$$(H, H, C_6 H_7) N = C_6 H_9 N = 3(C_2 H_3). N.$$
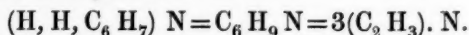
The interesting observation likewise made by Wertheim, that the so-called propylamine exists in considerable quantity in herring-brine, has afforded an opportunity of putting this question to the test of experiment. At Dr. Hofmann's suggestion, the subject has been examined by Mr. Henry Winkles, from whose experiments it appears that the principal constituent of a mixture of bases contained in herring-brine is actually *Trimethylamine.* The base was identified both by comparison with trimethylamine synthetically prepared, and by its behaviour with iodide of methyl. With the latter it instantly solidified into a crystalline mass of iodide of tetramethylammonium.

From these experiments it seems doubtful whether the true *Propylamine* has yet been obtained. It would also be as well to examine by experiment whether *Petinine* is really entitled to the name of *Butylamine.* This question might be easily decided by the behaviour of petinine with iodide of methyl or iodide of ethyl.

* Ann. Ch. Pharm. LXXXIII, 116.   † Ibid. LXXIX, 29.

XXIII.—*On the Action of Iodine upon Phosphorus.*

BY B. C. BRODIE, F.R.S.,

SECRETARY OF THE CHEMICAL SOCIETY.

The law of the formation of certain elemental bodies, which I have given in a former paper* suggests the probable cause of their allotropic differences.   For if it be proved that the formation of the element is a chemical synthesis of the same nature as the formation of a compound substance, we are enabled to transfer to the element those ideas of *form,* by which we most reasonably explain isomeric differences, and to comprehend that, in their case also, two or more substances may exist, identical in their ultimate chemical constitution, yet differing in the arrangement of their particles.

Considering how this view might be brought to the test of experiment, it occurred to me that there was a certain mode of effecting the isomeric transformation of compound substances of which as yet there was no example in the case of the elemental bodies, and which appears to me essentially to depend upon the peculiar chemical nature of the change produced.   I speak of that continuous chemical action by which sulphuric acid converts aldehyde into a body isomeric with it, but of triple its atomic weight, and by which the same acid transforms oil of turpentine into the remarkable series of isomeric hydrocarbons investigated by Deville.

* Chem. Soc. Qu. J. IV, 194.

A fact which had been observed in the action of iodine upon phosphorus seemed to indicate what I sought. In various experiments in which these substances had been brought together, a certain red body had been observed, resembling the allotropic phosphorus, the origin and true nature of which was unexplained. Thus, for example, Berzelius* remarks that if less be taken than six parts of iodine to one of phosphorus, the phosphorus separated is in the state either of oxide or of the modification produced by sunlight. Recently, Mr. Corenwinder,† in his investigation on the iodides of phosphorus, observed that when iodine and phosphorus were dissolved in bisulphide of carbon, if more than a certain proportion of phosphorus was employed, a matter of the same appearance was produced on evaporating the solution.

The action of iodine upon phosphorus is, as is well known, very violent; therefore the better to investigate the nature of the experiment I dissolved the iodine and phosphorus in bisulphide of carbon, evaporated the solution to dryness in the method above mentioned, and carefully washed out the residue thus obtained with bisulphide. This residue has much the appearance of the allotropic modification; but on examining its nature more closely, I discovered that a large proportion of iodine was retained by the phosphorus in a form insoluble in bisulphide of carbon. It was evident that some peculiar iodide of phosphorus was formed. My efforts, however, to separate any substance in a pure state, or indeed to obtain in this manner any constant results whatever, failed.

It occurred to me that were I able to cause the formation of this iodide to take place in the fluid itself, it might separate free from the other matter which accompanied it, and in a condition in which it could be readily washed and purified. At the usual boiling-point of the bisulphide, the substance is not formed, but it was probable that at a higher temperature it might be produced. To make this experiment I placed the solution of iodine and phosphorus in bisulphide in tubes hermetically sealed, which I heated in a water-bath to 100° C. After a short time, a copious red deposit appeared on the sides of the tube. I used at first what appeared to me a great excess of phosphorus, 10 or 12 equivalents to 1 of iodine. The whole of the iodine was retained in the red substance. The filtered fluid contained unaltered phosphorus. The substance was dried in a current of hydrogen, and the phosphorus determined as pyrophosphate of magnesia. The

* Traité de Chimie, I, 247.
† Ann. Ch. Phys. [3] XXX, 242.

results which I obtained were very constant, different tubes gave very nearly the same amount of phosphorus, and I was inclined to believe that I had obtained the iodide in question, pure.   But closer examination proved that when the circumstances were sufficiently modified, very great variation took place in the results, and I arrived at length at the fact, that the amount of red phosphorus in the precipitate, increased directly with the proportion of phosphorus employed in the experiment.   Thus, for example, from a solution containing 12 equivalents of phosphorus to 1 of iodine, a substance was formed containing 68 per cent of phosphorus.   When the proportions were as 10 equivalents of phosphorus to 1 of iodine, the substance contained 66 per cent.   When as 4 equivalents to 1, 60 per cent.   When as $2\frac{1}{2}$ to 1, 58 per cent.   When as 1 to 1, 54·5 per cent of phosphorus.   These proportions vary from about 1 equivalent of iodine to 8 of phosphorus, to 1 equivalent of iodine to 5 of phosphorus.   The experiments are not perfectly comparable with each other, for there is another cause of variation, namely, *time*, which should be strictly taken into account. This, however, under the circumstances under which the experiments were made, has, I have ascertained, but a very small effect compared with the influence of mass.   The inference which I draw from these experiments is, not that this substance is a new sort of chemical combination in varying proportions, but that some definite iodide of phosphorus is present, accompanied by proportions of the allotropic phosphorus, which vary according to the circumstances I have mentioned, and from which by the similarity of its properties it cannot be separated.   I was very desirous of isolating this iodide, but my attempts to effect this have hitherto failed.

Cold water does not act on this substance; by boiling water it is slowly decomposed.   In caustic potash solution, phosphide of hydrogen is evolved, and the whole substance ultimately destroyed; but boiled with a solution of carbonate of soda, the iodide is decomposed with but little action on the phosphorus.   By far the greater part of the iodine can readily be thus removed, but slight traces so adhere to the phosphorus, that I have never succeeded in absolutely separating it.   A preparation thus made gave 94·9 per cent of phosphorus determined as pyrophosphate of magnesia.

Heated in a small tube, the substance appeared to distil unaltered. Like arsenic, it sublimed without melting, and presented the very peculiar appearance of that metal on sublimation, which is not easy to describe, separating from the sides of the tube in thin leaves. The sublimate was black, and of a semi-metallic lustre.   Making the experiment on a larger scale, I found, however, that it was by no

means unaltered; for the distilled substance washed with cold water gave a large quantity of hydriodic acid.

To examine the final result of this decomposition, several grammes of a substance which had been analysed were distilled from one end of a combustion tube to the other, the centre of the tube being filled with small pieces of pumice, heated red-hot with charcoal. A very high temperature is required for the distillation. The distilled substance, when cold, was broken from the sides of the tube, and at once extracted with bisulphide of carbon. The bisulphide dissolved a large quantity of the ordinary iodide of phosphorus, probably $I_2 P$, which, on evaporation, crystallized from the solution, and also a portion of ordinary phosphorus. The substance was now analysed. I did not bring it in contact with water, lest oxygen should enter into the substance at the moment of the decomposition of the iodide. Before the distillation, the body contained 67·3 per cent of phosphorus; it now contained 89·5 per cent. The experiment was repeated with the same substance. After this second distillation, it contained 95·5 per cent of phosphorus. It was plain that the effect of the distillation was to decompose the body with formation of ordinary iodide of phosphorus and the allotropic phosphorus itself.

These facts gave the key to the true nature of this change. It became evident to me that it belonged to that class of infinite chemical actions to which I have before alluded. This is further proved by the following experiments.

A tube about half an inch wide, containing 16·9 grains of ordinary phosphorus, was filled with carbonic acid, and closed by a cork, and then placed in warm water at a temperature of about 40° C., so as just to melt the phosphorus. It was removed from the water, and 0·64 grains of iodine, being 1 equivalent of iodine to 100 equivalents of phosphorus, gradually projected into it. The iodine dissolved in the phosphorus, colouring it slightly red. The tube, closed by a cork, was heated gradually in an oil-bath, and examined as the temperature rose. At 100°, the colour became deep red; at 120° to 130°, a scarlet powder was deposited on the sides of the tube. Before 140°, the mass was quite solid. At about 200°, a sharp explosion took place with a loud report, driving the cork from the tube. The vapour inflamed at the mouth of the tube, but no portion of the substance was driven off. An intense heat had evidently been evolved. The substance was broken in various places, and traces of ordinary phosphorus distilled on the sides of the tube. Nearly the whole of the phosphorus used had passed into the allotropic modification.

To determine the quantity of phosphorus which could thus be converted by a given quantity of iodine, I made the following experiments in the manner just described, and after the action, broke out the substance from the tube, washed it carefully with bisulphide of carbon, dried it in a current of hydrogen, and weighed it. The whole of the iodine was always retained in the insoluble form. The amount of iodine used was deducted from the substance obtained, and the difference considered as the phosphorus converted. This method is of course rough, but it gives results sufficiently accurate to show the general law of the action. About 10 or 12 grains of phosphorus were usually employed in each experiment. In two experiments, strictly comparable, heated for the same time at the same temperature, in which 1 equivalent of iodine acted on 100 equivalents of phosphorus, 1 part by weight of iodine converted 19·85 and 19·45 parts of phosphorus, or 1 equivalent of iodine converted 78 equivalents of phosphorus. In four other experiments comparable with each other, in two of which 1 equivalent of iodine and 100 equivalents of phosphorus, and in the other two, 1 equivalent of iodine and 200 equivalents of phosphorus were employed. The results were as follows : in the two former, 1 part of iodine converted 21·6 and 24·0 of phosphorus, or 1 equivalent of iodine converted about 94 equivalents of phosphorus ; in the two latter, 1 part of iodine converted 29·32 and 27·91 parts of phosphorus, or 1 equivalent converted about 115 equivalents of phosphorus. In two other experiments made with 500 equivalents and 1000 equivalents of phosphorus, in the latter of which only about 0·008 grms. of iodine acted on 20 grms. of phosphorus, one part of iodine converted 64·8 and 99·62 parts of phosphorus, being as 1 to 257 and 395 equivalents. The greater part of the change is evidently effected at the moment when the principal evolution of heat takes place. But, as in the experiments with bisulphide, the quantity converted varies with the time, and there is every reason to believe, that taking this into consideration, the effect produced by the iodine is absolutely unlimited.

The change thus produced may be exhibited in various ways. When phosphorus is melted at the bottom of a flask filled with carbonic acid by a stream constantly passing through it, and iodine projected in very small quantities on the phosphorus by means of a long tube inserted in the cork and reaching nearly to the bottom of the flask, with both extremities open, a violent action takes place, attended with the production of intense heat. After the experiment, the substance appears as a very hard semi-metallic black mass, giving

a red powder. In this way, at least 30 grms. of phosphorus may be operated upon with safety.

The same experiment may be made under certain liquids which do not act upon the iodide. Water cannot be used, but the experiment succeeds with very concentrated hydrochloric acid. A small quantity of phosphorus was just melted in a test-tube under the acid, and a weighed quantity of iodine projected into it. The iodine dissolved in the phosphorus colouring it deep red; but after the addition of a certain quantity of iodine the substance appeared to explode, and the whole mass was converted into the hard black substance before described. The quantity of iodine projected into the phosphorus before the change, was about 1 equivalent of iodine to 1 of phosphorus. The experiment is best made by first carefully adding the iodine to the phosphorus, and then heating over a lamp until the explosion takes place.

The peculiar phenomena which the distillation of the red phosphorus containing the iodide, as prepared from bisulphide of carbon, presented, induced me to make the following experiments. About 42 grms. of phosphorus were carefully melted at the end of a long combustion-tube, and 1·6 grms. of iodine, being in the proportion of 1 equivalent of iodine to 100 of phosphorus, gradually, as before, projected into it. The phosphorus was converted by heating, first to 100° C., at which temperature it solidified, and afterwards in a trough of sand heated to about 200°. The change on removal to the sand was most remarkable. The conversion of the phosphorus could distinctly be followed from one end of the tube to the other. There was evidently a great evolution of heat, and the phosphorus broke up into a series of solid rings. The tube, when cold, was removed to a combustion-trough; the space immediately before the phosphorus heated very hot with charcoal; and the phosphorus distilled to the other end of the tube through the heated part. After the experiment, the phorphorus was found condensed on the sides of the tube, and nearly filling it, as a very hard black mass. Great care is required so to conduct the distillation as not to stop up the tube. The distilled substance contained traces of the ordinary phosphorus, but nearly the whole was in the allotropic form. The allotropic phosphorus passes by distillation into the usual modification, and a curious point suggests itself, whether in this experiment in the presence of the iodine, the allotropic phosphorus distils unaltered, or whether it is altered by distillation and reconverted by the iodide of phosphorus which distils with it. I cannot give a satisfactory answer to this question; but the very peculiar way in which,

as I have before mentioned, like arsenic, the phosphorus sublimes, inclines me to the former view.

The allotropic phosphorus, as prepared by iodine, presents certain differences with the phosphorus converted by heat, which led me at first to doubt whether they were the same substance. It was much more readily acted upon by potash, and precipitated certain metallic solutions—for example, sulphate of copper—in a way which the other phosphorus did not. It slightly lost weight also on drying in a current of hydrogen at 100°, which is not the case with the other phosphorus. My opinion now is, that these differences arise from the presence in the phosphorus of a small quantity of iodine and possibly also of oxygen (if it has been boiled with water), which adhere pertinaciously to the substance. We know that in many cases the presence of small quantities of foreign matter alters materially chemical reactions. The experiments, however, which I made, with the view of ascertaining this point, have some value. I oxidized the phosphorus by boiling with aqua-regia, in the presence of a small quantity of nitre, and repeatedly evaporated to dryness, to ensure the conversion of the whole substance into phosphoric acid, which I determined as pyrophosphate of magnesia. In the two following experiments, a preparation of phosphorus, made by distillation of the iodide, was further purified by boiling for three days in a retort with water, and afterwards drying *in vacuo*. The substance on the filter washed with boiling water, gave no trace of iodine. This substance thus determined, gave a quantity of pyrophosphate, corresponding in two experiments to 101·8 and 100·6 of phosphorus in 100 parts of the original substance. Two experiments with another preparation gave 100·06 and 99·390 per cent, assuming, that is, the equivalent of phosphorus as 32, and that of magnesia as 12·2. Three comparative experiments, made with the allotropic phosphorus converted by heat, gave 105·36—105·84 and 105·51 of phosphorus in 100 parts of the original substance on the same assumption, giving a mean of 105·57 per cent. An experiment with the ordinary phosphorus, with which, for obvious reasons, the result may not be quite so accurate, gave 104·57 per cent of phosphorus in 100 parts. The determination with pyrophosphate of magnesia, made with care, gives most concordant results; and I have no doubt but that the apparent anomaly of the experiments arises from the assumption of a wrong atomic weight of phosphorus. The recent experiments of Schrötter[*] have given 31 for its equivalent

* Ann. Ch. Pharm. LXXX, 202.

number. The mean of the three experiments with the allotropic phosphorus above given, requires 30·31. The subject requires further investigation.*

I compared also the specific gravity of the two preparations. It was taken in bisulphide of carbon, of which the specific gravity was taken immediately after the experiments. Two experiments with the phosphorus prepared by iodine gave a specific gravity of 2·22 and 2·24, mean 2·23. Three experiments with the phosphorus prepared by heat gave 2·14, 2·13, 2·14 specific gravity, mean 2·14. The density of this substance, determined by Schrötter† at 10°, is 1·964. My determinations, however, are likely to be more accurate, as Schrötter took the density in water, with which the phosphorus cannot be wetted. Assuming this density and the above equivalent number 30·3, the atomic volume of phosphorus $= \dfrac{378}{2·14}$, becomes 176, being nearly the same as that of arsenic, which is 167.

In the preceding experiments, I have not only shown the result of this action of iodine upon phosphorus, but have analysed the process by which this result is produced. I consider that it may be accounted for by the known laws of chemical action. The first step in the series of changes is the combination of iodine and phosphorus, in which most probably the substance described by Corenwinder, I_2P, is produced. The next is the conversion of this substance into the allotropic iodide; and the third, the decomposition of this iodide, with the formation from it of the allotropic phosphorus and a volatile iodide, which decomposition takes place more or less rapidly, according to the temperature. This volatile iodide reacts in a similar manner upon a further portion of phosphorus, and thus the action is infinitely continued. By modification of the process, it may be arrested at any one of these stages.

The time at which the phosphorus truly undergoes the molecular change, appears to me to be the moment of its second combination with the iodine. I consider it as contained in its altered condition in the substance then produced, and I regard the allotropic phosphorus as the product of the decomposition of this body. There are facts similar to this decomposition in the case of other elements. The sulphur formed by the decomposition of chloride of sulphur by ammonia is in the insoluble form. The decomposi-

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* In the determinations elsewhere given in this paper, the atomic weight has been taken as 32.

† Ann. Ch. Phys. [3] XXIV, 417.

tion of the selenide* of potassium and of ammonium by water, produces allotropic selenium. From the description given by Sacc,† the same body appears to be formed by the decomposition by water of the liquid chloride of selenium. I know, however, of no other case in which the action is continued.

The iodide of phosphorus, which plays so important a part in the change, nearly disappears in the final result. In the phosphorus distilled with iodine, only traces of it remain. From this we can readily understand how in other cases chemical results may be brought about by means of intervening steps and by the formation of substances of which no trace whatever is ultimately left. This hypothesis has already been to some extent applied to give a rational view of certain chemical changes which could not otherwise be accounted for, but has never received that development in the philosophy of chemistry to which it appears to me to be entitled.

XXIV.—*On the Valuation of Indigo.*

By Dr. Frederick Penny, F.C.S.,

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Several methods have been employed for estimating the comparative value of commercial indigo.

The colorimetric processes with chlorine, proposed by Berthollet, and first practically applied by Descroizilles, have been most extensively tried, and have been fully described by Berzelius,‡ Chevreul,§ Schlumberger,‖ Schubart,¶ Persoz,** and others. In these processes chlorine-water or bleaching-powder was used as the source of the chlorine.

Bolley†† has proposed chlorate of potash and hydrochloric acid as the source of chlorine, and has reported very favourably of

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* Chem. Soc. Qu. J. V, 93.
† Ann. Ch. Phys. [3] XXXII, 385.
‡ Traité de Chimie.
§ Leçons de Chimie appliquée à la Teinture.
‖ Bullet. de la Soc. Industr. XV, 277.
¶ Tech. Chimie.
** Traité de l'Impression des Tissus.
†† Ann. Ch. Pharm. 1850.

the results obtained by operating upon specimens of various qualities.

Some chemists consider that the only method of accurately determining the value of this article consists in removing the various impurities by the successive action of diluted acid, caustic alkali, alcohol and water, and then ascertaining the quantity of indigo-blue that remains, the ash being deducted in the usual manner. Others, again, prefer the process of reducing the indigo-blue by deoxidizing agents, and afterwards precipitating and collecting it in the pure state. This method was, about the commencement of the present century, adopted by Pringle,* who employed the well-known materials, sulphate of iron and lime, as the reducing and dissolving agents, and separated the indigo-blue from the clarified solution with hydrochloric acid. The operations involved in this process are exceedingly tedious, and in consequence of the peculiar property which reduced indigo has of forming two distinct combinations with lime, the one soluble, and the other insoluble (a fact not known to Pringle), the results afforded by it are not always satisfactory.

Dana† has recommended another method, based, however, on the same principles. It consists in boiling the indigo in caustic soda, and cautiously adding protochloride of tin until the indigo-blue is completely reduced and dissolved; the clear solution is then precipitated by bichromate of potash, and the precipitate being well washed with dilute hydrochloric acid, is dried and weighed.

Fritzche‡ has suggested cane-sugar, alcohol and caustic soda for the reduction and solution of the indigo-blue. His process, which appears, however, to be better adapted for the preparation of pure indigo, than for testing its value, has been repeated and favourably spoken of by Marchand; and Berzelius says that it surpasses all other methods that have been employed for obtaining indigo-blue in . a state of purity.

Chevreul's method of dyeing cotton until the indigo-solution is exhausted is obviously very objectionable.

Reinsch,§ after trying various modes, prefers that of dissolving a grain and a half of the indigo in concentrated sulphuric acid, and then estimating its comparative value by the quantity of water required to be added to reduce the colour of the solution to a certain shade. This process, which is simple and convenient, is in every respect similar to

* Annales des Arts et Manufac. VI, 214—239.

† J. pr. Chem. XXVI, 398.

‡ J. pr. Chem. XXVIII, 16.

§ Jahrb. prak. Pharm.

that long since applied by Ure,* though Persoz† ascribes it to Houton-Labillardière.

The advantages and disadvantages of these processes have been so fully discussed by Bolley in his paper, before referred to, that it is unnecessary, I conceive, to make any further comment on their respective merits.

The method I have now to propose, is based upon the circumstance that indigo-blue in presence of hydrochloric acid, is decolorised by bichromate of potash. This salt has long been used for discharging indigo-blue and other colours in the printing of textile fabrics, as well as for bleaching oils, fats, and several other substances. In employing it for estimating the comparative value of commercial indigo, the necessary manipulations are extremely simple.

Ten grains of the sample, in very fine powder, are carefully triturated with two drachms by measure of fuming sulphuric acid, and the mixture being excluded from the air is allowed to digest with occasional stirring for twelve or fourteen hours. A small flat-bottomed flask with a tightly fitting cork, is a very convenient vessel for this operation. Some pieces of broken glass should however be thrown in to facilitate the contact of the indigo and acid during the agitation, and thus to prevent the aggregation of the former into small clots, which the acid by itself cannot penetrate. If a small capsule or testglass be used, it should be covered, during the digestion, with an airtight gas-jar. It will also be found advantageous to place the mixture in a warm situation, say between 70° and 80° F., that the action of the acid may be fully developed; a higher temperature than this must be avoided, as sulphurous acid is liable to be produced, and the trial in consequence completely vitiated. Great care must be taken to insure the perfect solution of the indigo-blue in the acid. This result being accomplished, the solution is poured slowly, with constant stirring, into a pint of water contained in a basin, and ¾ of a volume ounce of strong hydrochloric acid immediately added, the flask or capsule being rinsed clean with water.

An alkalimeter of 100 equal measures, is now made up in the usual way with 7½ grains of dry and pure bichromate of potash, and the solution added in small successive portions to the diluted sulphate of indigo in the basin, until a drop of the mixture, on being let fall on a white slab or slip of bibulous paper, presents a distinct light brown or ochre shade, unmixed with any blue or green. The process is then

* J. Roy. Inst. 1830.
† Traité des Tissus, I, 434.

finished ; the number of measures of bichromate used is read off, and this number shows the comparative value of the indigo subjected to the trial.

In applying the test-drop to the bibulous paper, the best results are obtained by bringing the end of a glass rod into contact with the indigo-solution, and then gently pressing it against the surface of the paper. The stain thus produced will be circular and conveniently localised to a small space. By using bibulous paper it will also be found much easier to recognise the last traces of the blue colour than when a slab is employed, and the results, when dry, may be preserved unchanged for reference or comparison.

It is advisable to keep the indigo-solution gently heated while the chrome-liquor is being added ; and it is essentially necessary that the mixture should be well stirred after each addition. Several measures of the chrome-solution may at first be poured in without risk of error, but towards the conclusion, the liquor must be added very slowly and with great care, as one or two drops will then be found to produce a very decided effect. The characteristic changes of colour which the mixture undergoes during the addition of the chrome-solution, will distinctly indicate the approach of the process towards conclusion. The blue colour of the solution gradually diminishes in intensity, becoming perceptibly lighter and lighter, and after a time it acquires a greenish shade, which soon changes to greenish-brown, and almost immediately to light ochre-brown.

I have tried this process very carefully upon pure indigo, prepared according to Fritzche's method. The mean of three experiments, which gave results almost identically the same, showed that 10 grains of pure indigo require very nearly $7\frac{1}{2}$ grains of bichromate of potash ; and I have accordingly taken this quantity of the salt for solution in the alkalimeter.

The following table contains the results of trials upon three series of specimens of commercial indigo, and includes likewise the price of each sample, and the amount of ash left after careful incineration, as well as the moisture expelled at 212°. The first series of samples was. obtained from an indigo broker, in London ; the second from Messrs. C. Tennant & Co., Glasgow ; and the third from Messrs. R. and I. Henderson, Glasgow.

FIRST SERIES.

SPECIMENS.	Price, 1851.		Alkalimeter measures consumed.	Ash per cent.	Water per cent.
	s.	d.			
East Indian . . .	6	4	68	4·5	5·0
,, ,, . . .	6	0	66	5·8	6·0
,, ,, . . .	5	9	64	8·1	8·0
,, ,, . . .	5	6	54	11·0	7·0
,, ,, . . .	4	9	51½	7·2	7·5
,, ,, . . .	4	8	54	3·6	7·0
,, ,, . . .	4	4	45	14·0	8·4
Spanish	4	3	55	12·3	6·0
,, ...	3	10	50	13·0	7·0
,, ...	3	6	44½	19·0	5·5
,, ...	2	10	28	33·4	4·5

SECOND SERIES.

SPECIMENS.	Price, 1851.		Alkalimeter measures consumed.	Ash per cent.	Water per cent.
	s.	d.			
Bengal	5	0	64	5·9	4·0
,, ...	4	9	47	24·6	5·0
Benares	4	6	45	20·7	8·4
Guatemala . . .	4	3	50	16·0	6·5
Madras	3	8	41	10·6	6·7
Oude	3	8	46	6·3	8·5
Caraccas	3	6	52½	16·2	6·4
Madras	2	9	35	33·3	6·0

THIRD SERIES.

SPECIMENS.	Price, 1852.		Alkalimeter measures consumed.	Ash per cent.	Water per cent.
	s.	d.			
Java	5	6	63½	5·4	4·8
Bengal	4	10	59½	7·5	5·0
,, ...	4	0	56	11·0	5·3
,, ...	3	4	45½	14·0	7·2
,, ...	1	6	24	44·4	4·4
Manilla	3	4	35½	28·0	5·0
,, ...	2	0	26½	50·0	5·4

The results in these tables clearly show the uncertainty, and in several instances the positive inaccuracy, of the common methods at present employed by commercial men for estimating the true value of this article.   The indications of quality afforded by colour, fracture, texture, coppery hue when rubbed, cleanliness, weight, and other characters, should always in my opinion be confirmed by the application of a simple chemical process, such as I have here described.   The objection on the score of the time consumed, so strongly urged against many of the other methods, is certainly not chargeable against this ; for, by steeping the indigo in the acid overnight, twenty or thirty samples at least could be easily tested in a day, and at a trifling expense.

I may mention that there was recently sent me for examination a specimen of indigo, offered in Glasgow as refined indigo, at 10s. per lb.   It gave 9 per cent of ash, and $2\frac{1}{2}$ per cent of moisture; and 10 grains, when dissolved in sulphuric acid, consumed 82 measures of the bichromate of potash solution.   It is in very fine powder, with a deep coppery-blue colour.   Assuming its quality and purity to be uniform, it would unquestionably be more economical, even at the high price of 10s. per lb., than much of the indigo at present sold.   Its tinctorial powers could be relied on ; and from the circumstance of its being finely pulverized, it obviously admits of being rigorously tested by the bichromate process.

The method here proposed is open, I am well aware, to some of the many objections that have been advanced against the well-known chlorine process.   It is quite obvious, for instance, that unless particular care is taken in dissolving the indigo in the sulphuric acid, not only is a part of it liable to escape solution and proper estimation, but in the case of inferior indigo, sulphurous acid may be produced, which would of course involve a larger consumption of the bichromate of potash than the indigo-blue itself would require.   It may also be objected that bichromate of potash, in the presence of hydrochloric acid will act upon the other constituents of ordinary indigo; but so far as I have been able to judge from a very extensive course of experiments upon a great variety of specimens, the amount of these influences is extremely slight, and altogether inappreciable when the process is executed with proper care.   The same opinion has been expressed by Berzelius and Schlumberger regarding the chlorine process ; and it is further supported by the fact, that indigos containing a large proportion of brown and other colouring matters, consume a very small quantity only of the bichromate.   While, therefore, this process has no pretensions to supply scientific men

with the means of determining the actual amount of pure indigo-blue in samples of commercial indigo, it is in my opinion admirably adapted for ascertaining their relative values, being in many respects superior to those which have hitherto been proposed.

The bichromate of potash possesses in an eminent degree all the qualities requisite for a trustworthy agent of valuation, being easy of purification, unchangeable by keeping, and of uniform composition.

XXV.—*On the Constitution of Stearine.*

By Patrick Duffy.

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A specimen of stearine from mutton fat, having its second melting-point at $62°·5$, and, therefore, nearly identical with the substances analyzed by Lecanu* and Heintz† respectively, burned with chromate of lead, gave the following results:

I. 0·2989 grm. gave:
   0·8483 ,,   carbonic acid, and
   0·3277 ,,   water.
II. 0·2706 ,,   gave:
   0·7677 ,,   carbonic acid, and
   0·3026 ,,   water.
III. 0·2670 ,,   gave:
   0·7544 ,,   carbonic acid, and
   0·2941 ,,   water.
IV. 0·2820 ,,   gave:
   0·7943 ,,   carbonic acid, and
   0·3148 ,,   water.
V. 0·3492 ,,   gave:
   0·9858 ,,   carbonic acid, and
   0·3858 ,,   water.

These numbers correspond to the following quantities per cent:

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* J. Pharm. [3] XX, 325; Ann. Ch. Phys. [2] LV, 192.

† Pogg. Ann. LXXXIV, 229. It is, perhaps, proper to state that it differed from theirs in being the second crop of crystals in the twenty-fifth ethereal solution of mutton fat, instead of the first crop in the sixth or seventh solution.

	I.	II.	III.	IV.	V.
C.	77·40	77·37	77·05	76·81	76·99
H.	12·18	12·42	12·23	12·40	12·27
O.	10·42	10·21	10·72	10·79	10·74

The following are the numbers obtained by Lecanu and Heintz, also the melting-point given by them. Liebig and Pelouze do not mention the melting-point of the stearine analyzed by them, and Artzbächer's melted at 60°·6, so that a comparison of their results with the others is not admissible.

	Lecanu.	Heintz.	Mean of mine.
Second melting-point	62°	62°	62°·5
C. . .	76·90	76·74	77·12
H. . .	12·44	12·42	12·30
O. . .	10·66	10·84	10·58

1·8297 grm. of this substance was saponified in a small flask by a solution of potash in alcohol; the alcohol nearly all distilled off in the water-bath; and water added, which formed a clear solution of the soap. This solution was heated in the water-bath till all smell of alcohol disappeared; the soap was decomposed by dilute sulphuric acid in slight excess, the liberated fatty acid allowed to collect and solidify; and the water containing the sulphate, or sulphoglycerate of potash, removed by a delicate pipette: it was slightly opalescent from precipitation of a small quantity of silica, which the potash had removed from the flask. The fatty acid was afterwards washed, till the washings ceased to leave any residue on evaporation, and till the acid ceased to lose weight by washing, and subsequent drying at 100°. It then weighed 1·7521 grm.

In a second similar operation, 1·4056 grm. of stearine afforded 1·3426 grm. of acid.

In a third operation, 1·0399 grm. of stearine afforded 0·9931 grm. of acid. A determination of the glycerine produced in this operation was also made; for that purpose, the solution of sulphate of potash, mixed with glycerine, was evaporated by a steam-heat nearly to dryness; dry carbonate of potash added; the glycerine extracted by absolute alcohol; and the alcoholic solution was filtered and evaporated over sulphuric acid in the air-pump vacuum till it ceased to lose weight. From the weight so obtained, was deducted that of the small quantity of sulphate and carbonate of potash left on burning off the glycerine. The glycerine weighed 0·093 grm.

The acid of each operation was fusible at 64°·7 into a perfectly limpid liquid.

These quantities compared to 100 parts of the stearine are as follows:

	I.	II.	III.	Mean.
Acid . . .	95·76	95·51	95·50	95·59
Glycerine . .	—	—	8·94	8·94

The acid, burned with chromate of lead, gave the following results:

> I. 0·2969 grm. of first operation gave:
> 0·8258 ,, carbonic acid, and
> 0·3320 ,, water.
> II. 0·3164 ,, of second operation gave:
> 0·8787 ,, carbonic acid, and
> 0·3572 ,, water.

These numbers correspond to the following percentages:

	I.	II.	Mean.
C.	75·85	75·74	75·79
H.	12·42	12·54	12·48
O.	11·73	11·72	11·73

The equivalent weight* of the acid was determined from its silver and soda salts. A portion of the acid was added to a solution of pure carbonate of soda, which was boiled till saponification was complete, and then evaporated to dryness; the resulting soap was removed from the excess of carbonate of soda† by treatment with boiling absolute alcohol and filtration; the alcoholic solution of soap was evaporated to dryness, and the remaining soda-salt dissolved in water; and from this solution the silver-salt was prepared by precipitating with nitrate of silver, washing the precipitate, and drying at 100°, keeping it protected as much as possible from daylight.

0·5893 grm. silver salt of acid of first preparation left on ignition 0·1638 grm. silver.

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* The term "equivalent weight," is here used in preference to that of "atomic weight," as the latter is not strictly applicable in respect to substances consisting of a mixture. In some instances in this paper, where this reason for its use does not apply, it has been retained for the sake of uniformity. Another reason was, that in speaking of equivalents it was not required to take into consideration the fact of the acid being bibasic, which would only have complicated the remarks that follow.

† Carbonate of soda dissolves in small, but, for questions of atomic weight, important quantities, in absolute alcohol; but I have some reason to think that it is quite insoluble in an alcoholic solution of soap, which is just the opposite of what occurs with aqueous solutions, for here the carbonate of soda renders the soap insoluble. I had not an opportunity of fully investigating this point.

I. 0·4102 grm. soda salt of acid of second preparation afforded :
   0·0986   ,,   sulphate of soda.
II. 0·3415   ,,   of same salt afforded :
   0·0811   ,,   sulphate of soda.

A mixture of acids, of which 4 equivalents consist of 3 equivalents of stearic acid ($C_{34} H_{34} O_4$), and 1 of oleic acid ($C_{36} H_{34} O_4$), would require the following percentages :

	Calculated	Found.
C.	75·82	75·79
H.	12·45	12·48
O.	11·73	11·73

and in its salts :

	Calculated.	Found. I.	II.
Silver . .	28·42	27·79	—
Sodium . .	7·89	7·85	7·76

It is not intended to be implied that the acid analysed actually consisted of stearic and oleic acids in the proportions indicated ; on the contrary, it must have contained, if any, only a trace of oleic acid ; the assumed mixture is taken only for the convenience of calculation, inasmuch as its composition and equivalent weight closely represent those found.

100 parts of the fat contained 77·12 of carbon; the 95·62 parts of acid derived from them contained 72·44 parts of this carbon; the difference, viz., 4·68, is all that went to form glycerine.

The equivalent weights of the fat and acid are obviously in the proportion of 100 : 95·62, but the equivalent weight of the acid, according to the foregoing determinations, is 273 ; hence, the equivalent weight of the fat must be 285, which agrees with what we might deduce directly from its own analysis.

It has hitherto been supposed that any fat, such as stearine, which on saponification is resolved into a certain acid and glycerine, consists of this acid combined with a hypothetical base, oxide of lipyl ($C_3 H_2 O$) ; and that the process of saponification is merely a case of substitution, 1 equivalent of the alkali or other oxide employed, changing places with 1 equivalent of the oxide of lipyl, and combining with the acid to form soap, while 2 equivalents of oxide of lipyl, together with 4 equivalents of water combine to form hydrated glycerine ($C_6 H_8 O_6$).

If this represented what took place in the present instance, the loss of carbon sustained by the fat on being converted into acid, should have been to the fat, in the proportion of 3 equivalents of carbon to 1 of fat, or $\frac{18}{285} = 6\cdot31$ per cent of the fat. The actual loss was, however, only 4·65 per cent, a result which coincides closely with those found by Chevreul* in similar analyses of mutton, pork and human fats, each in the crude state. These fats, on being converted into acid, lost respectively 4·181, 4·685, 4·493 per cent of carbon.

Inasmuch as these fats were analysed by Chevreul in the crude state, while that which I operated upon was comparatively pure, it might be thought that, the conditions being thus different, any coincidence in the results can only have been accidental, and may have originated in a different source from that supposed, but Chevreul has left numerical data sufficient for making the calculations here required independently of the contrary hypothesis.

The crude acid which he obtained from these fats, when heated with oxide of lead, lost in each case the same quantity of water, viz., 3·65 per cent; its equivalent weight was therefore 246; consequently, the equivalent weights of the several fats were to 246 in the proportion of 100 to the percentage of acid obtained from them respectively, or as 100 : 96·5 for the mutton fat, 100 : 95·9 for the pork fat, and 100 : 96·18 for the human fat; that is, as 254, 256 and 255 respectively. Now, if 1 equivalent of each of these fats, on being converted into acid, had lost 3 equivalents of carbon, the difference between the quantity of carbon in 100 parts of the fat, and that in the percentage of acid obtained from it, should have been : in the case of the mutton fat, $\frac{18}{254} = 7\cdot08$ per cent, in the case of the pork fat, $\frac{18}{256} = 7\cdot03$ per cent, and in the case of the human fat $\frac{18}{255} = 7\cdot05$ per cent.

If we admit that the proportion of the fat, which in saponification goes to form glycerine, contains not 3, but 2 equivalents of carbon, we come much nearer the actual result. The agreement between the calculated and found quantities is then as follows :

	Calculated.	Found.	Glycerine found represents
Purified mutton fat . .	4·21	4·68	3·498
Crude mutton fat . .	4·72	4·181	3·130
„ pork fat . . .	4·68	4·685	3·451
„ human fat . .	4·70	4·495	3·780

* Rech. Chim. sur les Corps Gras, Paris, 1823, 333—343.

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Further, upon the lipyl theory, the difference between a fat and the hydrated acid producible from it, is that the latter contains 1 equivalent of water (HO), instead of 1 equivalent oxide of lipyl (C_3H_2O) in the former; consequently, the oxygen in an equivalent of either should be the same; but the analyses do not support this view. The oxygen found in 100 parts fat and their equivalent of acid is as follows:

	Purified mutton.	Crude (Chevreul):		
		Mutton.	Pork.	Human.
Acid . . .	11·21	10·132	10·253	10·633
Fat . . .	10·58	9·304	9·756	9·584
Excess in acid	0·63	0·828	0·497	1·049

According to these experiments, the acid did not derive all its oxygen from the fat. Is the excess only apparent, and belonging really to the errors of experiment; or is it due to the circumstance of any oleic acid present in the acid undergoing oxidation during the operations of drying, weighing, &c.; or does it represent a definite quantity of oxygen taken up in the form of water during saponification? The latter is most probable; for, firstly, the concordance of all Chevreul's analyses with mine in showing an excess, would probably not have occurred, if it had been due to accident. Secondly, there must have been extremely little oleine in the fat, and a correspondingly small quantity of oleic acid in the acid which I operated upon; and if it had arisen from the absorption of oxygen by any oleic acid possibly present, this absorption being gradual would have been discovered by a gradual increase of ·007 to ·01 grm. in the weight of the acid in my determinations; but although the acid was kept melted and exposed to the air for hours, no increase of its weight occurred. Thirdly, Chevreul's experiments* show that free oxygen is not taken up in saponification; the only remaining source of this increase is therefore the water used. Other experiments, to be mentioned presently, show that when alcohol is used instead of water, saponification does not occur in the ordinary way.

Upon the supposition that in the formation of 4 equivalents of acid there is taken up 1 equivalent of water, I should have found the increase of oxygen 0·70 per cent; and in the fats analyzed by Chevreul it should have been 0·78 per cent for each.

As to the relation between the hydrogen in the fat and that in the acid, it is scarcely possible to arrive in this manner at any definite

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* Rech. Chim. sur les Corps Gras, 323—329.

expression for it; for where a single equivalent of it does not, as in the present instance, amount to more than $\frac{1}{285}$th part of the substance, ordinary analysis can hardly decide between one equivalent more or less. The hydrogen in 100 parts fat, and in their equivalent of acid, appears from the analyses, as follows:

	Purified mutton.	Crude (Chevreul):		
		Mutton.	Pork.	Human.
Fat . . .	12·30	11·700	11·146	11·416
Acid . . .	11·93	11·553	11·234	11·040
	0·37	0·147	−0·088	0·376

With the exception of that of the pork fat, these analyses concur to show that the fat, on being converted into acid, loses hydrogen; the analysis of the pork fat shows an increase of 0·088 per cent in the acid.

Upon the supposition that the fat contains 1 equivalent of hydrogen more than the acid, I should have found a difference of 0·35; but this theoretical difference is reduced to 0·26, if we admit that the increase of oxygen has been taken up as an equivalent of water in the formation of 4 equivalents of acid. The hydrated acid contains 1 equivalent of basic hydrogen, which it did not derive from the fat; hence the conclusion is, that the part of the fat which goes to form the acid contains 2 equivalents of hydrogen less than the fat itself.

What I consider particularly established by the foregoing facts is, that an equivalent of fat, in being converted into one of acid, loses 2 equivalents of carbon; and that a given quantity of acid contains more oxygen and less hydrogen than the portion of fat from which it is derived.

Liebig and Pelouze* represented stearine by the formula 2S̄t, GlyO, 2HO, regarding it as analogous to sulphoglyceric acid; but Heintz has already remarked that the analyses, from which this formula was deduced, are at variance with those made by Lecanu, Artzbächer and himself, and, I may add, with those which I have made.

I have also made the following analyses of mutton stearine, which, after thirty-two crystallizations from ether, melted at 52°, 64°·2 and 69°·7, and furnished an acid melting at 66°·5. Burnt with chromate of lead:

* Ann. Ch. Pharm. XIX, 264; J. pr. Chem. 173; Ann. Ch. Phys. [2] LXIII, 146.

I.   0·2760 grm. gave :
     0·7745   „   carbonic acid, and
     0·3050   ,. water.
II. 0·3081   „   gave :
     0·8652   „   carbonic acid, and
     0·3360   „   water.
III. 0·2689   „   gave :
     0·7218   „   carbonic acid, and
     0·2927   „   water.
IV. 0·2974   „   gave :
     0·8310   „   carbonic acid, and
     0·3256   „   water.
V.   0·2887   „   gave :
     0·8075   „   carbonic acid, and
     0·3106   „   water.

These numbers correspond to the following per cent :

	I.*	II.	III.	IV.	V.
C	76·53	76·56	76·02	76·20	76·28
H	12·27	12·11	12·10	12·16	11·95
O	11·20	11·33	11·88	11·64	11·77

The following analyses of beef stearine, having its several melting-points at 51°, 63° and 67°, were made with chromate of lead.

I.   0·4709 grm. gave :
     1·3264   „   carbonic acid, and
     0·5187   „   water.
II. 0·2873   „   gave :
     0·8098   „   carbonic acid, and
     0·3143   „   water.

These numbers correspond to the following quantities per cent :

	I.	II.
C	76·87	76·87
H	12·24	12·15
O	10·89	10·98

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* Analyses I. and II. were made of the substance after it had been dried at 100°; the others were made of the crystals from ether, after they had been dried over sulphuric acid in the air-pump vacuum till they ceased to lose weight. It is probable that the difference between the carbon in the two series of analyses, arose from the crystals in the latter case having retained a trace of ether, and hence, that the numbers in the first two analyses are most nearly correct.

Beef stearine has accordingly the same composition as mutton stearine. In beef stearine, having its second melting-point at 60°·6, Artzbächer* found 2 per cent more carbon. The difference in the purity, as indicated by the melting-point, of the substances which we analysed, cannot, I think, account for this discrepancy in our results. He has fallen into an error in supposing that his results agree with those of Chevreul and Lecanu; for in Chevreul's "Recherches Chimiques sur les Corps Gras," I can find no account of any ultimate analysis of either crude or purified beef fat; and Lecanu† appears to have analysed stearine from mutton fat only.

To 1·019 grm. of mutton stearine, having its second melting-point at 62°·5, and 3·075 grms. of pure oxide of lead in fine powder, absolute alcohol was added in quantity sufficient to dissolve the stearine readily when heated. The whole was kept boiling in the water-bath, and frequently agitated during four hours, the alcohol being replaced as it evaporated. At the end of this time the oxide of lead retained its yellow colour, and nearly the whole of the stearine was recovered unaltered, except for the admixture of a trace of impalpably fine oxide of lead. No lead-soap appeared to have been formed. The difference between the circumstances of this experiment and those of the ordinary process of forming lead-plaster, was that the water of the latter operation was replaced by alcohol, yet this was sufficient to prevent saponification.

The following experiment was performed before those already detailed, accordingly in the belief that the fats were analogous to ordinary salts, and that saponification consisted, as represented, in an exchange of places between the alkali employed and the oxide of lipyl or other base of the fat; the only question was, as to what this base was. The intention was to procure a body corresponding to ordinary glycerine, but in which the water taken up by the base of the fat, on its liberation and conversion into glycerine, should be substituted by ether.

The experiment consisted in acting in the first instance upon stearine by the compounds procured by the action of the alkali-metals on pure alcohol, which, from their analogy with the hydrates of the alkalies, have been called the ethylates of the alkalies by Dr. Williamson. Two grms. of sodium were dissolved in a quantity of absolute alcohol sufficient to dissolve 23·803 grms. of stearine, which were added. (The propor-

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* Ann. Ch. Pharm. LXX, 239; Compt. Rend. des Trav. de Chim. 1849, 343.
† J. Pharm. [3] XX, 325; Ann. Ch. Phys. [2] LV, 192.

tions of sodium and stearine are nearly those of equivalent quantities, the sodium being slightly in excess.)   The whole was boiled for some time, and on being allowed to cool, it stiffened into a jelly, showing that a soap had been formed; the alcohol was then distilled off in the water-bath, and the soap dissolved in water.   On the surface of the solution an oily stratum formed, which was removed by a pipette, washed with water, and the washings added to the solution of soap.   The soap, being decomposed by hydrochloric acid, the fatty acid was collected, washed, dried, and weighed; it amounted to 17·481 grms.   The oily substance when dried, weighed 5·571 grms.   A quantity of glycerine, which was not weighed, was found in the liquid from which the acid had been removed.   The oily substance solidified on cooling into a semi-transparent mass, melting again at 29°.   It dissolved readily in alcohol and ether.   By crystallisation, from the former, its melting-point was raised to 33°·7.   It did not crystallise from ether, was not sensibly affected by aqueous solution of potash, but was readily saponified by an alcoholic solution of potash.   On distillation, the temperature rose gradually to 224° C., the substance came over partially decomposed, and a black mass remained in the retort.

The crystals from alcohol, after being dried over sulphuric acid in the air-pump vacuum till they ceased to lose weight, gave the following results when burned with oxide of copper:

I. 0·3200 grm. gave:
   0·8980 ,,   carbonic acid, and
   0·3600 ,,   water.
II. 0·4255 ,,   gave:
   1·1720 ,,   carbonic acid, and
   0·4920 ,,   water.
III. 0·3273 ,,   gave:
   0·8999 ,,   carbonic acid, and
   0·3796 ,,   water.

These numbers correspond to the following percentages:

	I.	II.	III.
C. . .	76·53	75·12	74·99
H. . .	12·50	12·85	12·88
O. . .	10·97	12·03	12·13

Although the analyses are not satisfactory, there can be no doubt, after all these facts, that this is the same substance as the stearic

ether prepared by Redtenbacher.* In short, I prepared this substance in the same manner that he did; viz. by passing a current of hydrochloric acid gas into a solution of stearic acid in alcohol, and found all its physical characters the same as those of the substance prepared by the action of ethylate of soda upon stearine.

Here are the numbers obtained by Redtenbacher in the analysis of stearic ether:

$$
\begin{array}{llll}
\text{C.} & . & . & . & . & 76 \cdot 13 \\
\text{H.} & . & . & . & . & 12 \cdot 88 \\
\text{O.} & . & . & . & . & 10 \cdot 99 \\
\end{array}
$$

In order to determine whether any more volatile products were formed in this reaction, 0·8187 grm. of stearine was acted upon by a quantity of ethylate of soda containing 0·0772 grm. of sodium. The stearine was placed in a tube inside a small flask, in such manner that no communication occurred between the stearine and the ethylate of soda, till the flask was filled with alcohol vapour, and all the air expelled from it. The orifice of a conducting tube, inserted in the neck of the flask, was then introduced under a mercury barometer standing in a mercury trough; by a slight inclination of the flask, the melted stearine was allowed to flow out of the tube into the ethylate of soda, the heating being continued. By this arrangement, any gaseous products formed in the decomposition would have been collected above the mercury in the barometer, and have produced a depression corresponding to their elastic force; but there were none, unless alcohol vapour; for the depression of the column was only from 30°·15 inches before the operation, to 28°·6 after it, or 1·55 inch, the temperature being 20°; and the same depression exactly was produced by a few drops of alcohol admitted into another similar barometer. Stearic ether was found to have been formed.

When stearic acid is substituted for stearine in this reaction, no ether is produced. To a quantity of ethylate of soda, containing 0·02 grm. of sodium, 0·25 grm. of stearic acid was added; stearate of soda was the only product.

Amylate of soda was formed by adding 0·445 grm. of sodium to pure amylic alcohol, and to this 5·46 grms. of stearine were added; a quantity of oily substance was formed which, being freed from soap by washing, and from amylic alcohol by being heated in an oil-

* Ann. Ch. Pharm. XXXV, 51.

bath for some time at 185°, melted at 25°·5, and was in every respect similar to stearate of amyl prepared by passing hydrochloric acid gas into a solution of stearic acid in amylic alcohol. At temperatures below its melting-point, it was semi-transparent, soft and glutinous; above its melting-point, it passed into a clear transparent fluid; it was readily soluble in alcohol and ether; it solidified as a jelly on cooling its solution in the former by a freezing-mixture, but did not crystallise from either; it was not acted upon by aqueous solution of potash, but was readily converted by an alcoholic solution of potash, into stearate of potash and amylic alcohol, which then exhaled its well-known odour.

When palmitine was substituted for the stearine, a corresponding result was obtained. To 0·231 grm. of sodium in amylic alcohol 2·598 grms. of palmitine, having its second melting-point 61°, were added. After boiling for some time, a solution of chloride of calcium in amylic alcohol was added, which gave a precipitate; every trace of the amylic alcohol was afterwards driven off; nothing else escaped at the same time; the residue was digested successively with anhydrous ether, absolute alcohol, and water. The ether, when filtered and evaporated, left 0·693 grm. of a substance having a close resemblance to the stearate of amyl, but melting at 13°·5. Its solution in alcohol, when cooled by a freezing-mixture, became opaque and gelatinous, but not sensibly crystalline. It resembled in every respect palmitate of amyl, which I prepared in the ordinary way with palmitic acid from the same specimen of palmitine.

Burned with oxide of copper and chlorate of potash, 0·246 grm. gave 0·709 grm. carbonic acid and 0·286 grm. water, which correspond to the following numbers per cent:

	Found.	Calculated.
C_{42} . .	78·60	77·30
H_{42} . .	12·91	12·88
O_4 . .	8·48	9·82

The excess of carbon found may have arisen from the palmitine used containing oleine, or a trace of some other fat. I had not enough substance to repeat the analysis.

What was removed by treatment of the lime-soap with alcohol consisted of glycerine, a small quantity of palmitate of amyl, some palmitate of lime, and chlorides.

Water removed inorganic salts only.

When in these decompositions of stearine and palmitine, the proportion of sodium was increased beyond that of 1 equivalent, the quantity of ether obtained diminished, and eventually, with a quantity of sodium which was certainly not less than 2 equivalents, no ether was obtained.

I need hardly state that the effect was similar when ethylate of potash was used. A solution of anhydrous ammonia in absolute alcohol, and which from analogy is ethylate of ammonia, seemed to produce no change on stearine, even when boiled with it for some time.

Considering this reaction of importance with reference to saponification and the constitution of the fats, I have repeated it under every variation of circumstances deemed likely to elicit its explanation, but the preceding are the principal results obtained; and, although several probable reasons might be assigned for it, I know none that can at present be advanced with much confidence.

It is interesting to observe that, while the ethers formed by stearic and palmitic acids, with vinous alcohol, melted respectively at $33°·7$ and $21°·5$,* the corresponding ethers of these acids with amylic alcohol melted at $25°·5$ and $13°·5$; showing an elevation of melting-point with an increase of atomic weight in the acid, and a depression of melting-point with an increase of atomic weight in the alcohol. I was unsuccessful in the attempt to obtain those of methylic alcohol, by passing hydrochloric acid gas into a solution of the acids in purified wood spirit. Should the character alluded to be found to be an instance of a general law as regards the series of fatty acids, we might predicate that cetine and substances of its class are not ethers.

ACTION OF PERCHLORIDE OF PHOSPHORUS ON GLYCERINE.

The intimate connection between the subject principally discussed in this paper and that of the constitution of glycerine, obviously requires that any conclusion admitted of the former must be controlled by results established of the latter. The inferences to be drawn from the results obtained with stearine are not easily reconciled with what is at present admitted of the constitution of glycerine. For this reason, it was intended to investigate the action of perchloride of phosphorus on glycerine.

When glycerine is added to perchloride of phosphorus, a strong

* Frémy found palmitic ether, prepared by means of sulphuric acid, to melt about $21°$ (Ann. Ch. Pharm. XXXVI, 46).

heat is developed, the mixture becomes glutinous, and in the cold hard. On treatment with water, or better, with carbonate of soda, a substance considerably denser than water, and very like precipitated silica, is obtained. In performing the reaction, it is advisable to have the glycerine as concentrated as possible, to add it in small quantities to the perchloride, stirring the mixture after each addition, and to cease adding glycerine as soon as all the perchloride is decomposed. When the glycerine contains much water, or is added at once in large quantity, the perchloride is resolved chiefly into phosphoric and hydrochloric acids, which have the power of dissolving, and at the same time decomposing the new product afterwards formed. The operator must protect himself, particularly his eyes, from the action of the hydrochloric acid fumes necessarily produced in large quantity.

A portion of this new substance was washed till free from every trace of hydrochloric and phosphoric acids, then fused with pure soda; in the nitric acid solution of the fused mass, nitrate of silver gave a copious precipitate of chloride of silver. Nitric acid has very little action on it in the cold, but when warmed dissolves it readily. This solution, rendered alkaline by ammonia, gave no precipitate with sulphate of magnesia. It therefore contains chlorine, but no phosphorus. It dissolves readily in cold solution of potash, very slowly in boiling solution of ammonia, very slowly also in boiling solution of acetic acid; it is not reprecipitated from any of these reagents by neutralisation; it seems quite insoluble in alcohol and ether. Cold water does not act upon it; but when kept in boiling water, it is very slowly dissolved, being converted into a substance which, on evaporation of its solution, remained as a hard, perfectly transparent body, highly hygrometric, absorbing in a damp atmosphere in four days its own weight of water, and being converted thereby into a glutinous mass. The aqueous solution of this latter substance was found acid to test-paper, but gave no reaction for hydrochloric or phosphoric acid, and did not appear to decompose bicarbonate of soda. The hydrochloric acid solution of the original substance being neutralised, was examined for glycerine; it furnished none. Hydrochloric acid converts it probably into the same substance, as does water.

I was prevented from analysing these substances by the circumstance of my period of study terminating.

XXVI.—*On the compounds of several essential Oils with the Alkaline Bisulphites.*

By Cesare Bertagnini.

An inquiry into the deportment of a great number of essential oils with the alkaline bisulphites has led to the following results :

The volatile oils, having the characters of aldehydes, which are more generally known under the term of hydrides, such as hydride of benzoyl, salicyl, cuminyl, &c., and also the class of compounds, of which the aldehyde *par excellence* is known as the prototype, possess the property of readily forming crystalline compounds with the bisulphites of the alkalies.   These compounds are composed of 1 equivalent of the aldehyde, 1 equivalent of the alkaline bisulphite and a variable number of water-equivalents.

Experiments made with a very considerable number of essential oils not belonging to the family of aldehydes, have proved that they are not capable of forming similar compounds.

The compounds in question are readily produced by agitating the oils in the cold with solutions of the bisulphites, or by placing the oils in contact with the alkalies and passing a current of sulphurous acid through the liquids.   The white, brilliant, crystalline substances generated in this manner, are entirely insoluble in solutions of the bisulphites and in cold alcohol ; they dissolve with facility in water, and are readily decomposed by the action of acids and bases, and likewise by an elevation of temperature, the original aldehydes being reproduced.   The formation of these substances may be employed with great advantage in purifying aldehydes, when occurring together with other compounds, or in recognizing their presence in mixed liquids.

The following is a list of the combinations as yet analysed, together with their formulæ.

Compounds with:

Hydride of benzoyl . .	$NaO,$	$2\,SO_2, C_{14}\ \ H_6\ \ \ O_2 + 2\,Aq$

$$\text{Hydride of nitrobenzoyl} \begin{cases} NH_4O, 2\,SO_2, C_{14} \begin{Bmatrix} H_5 \\ NO_4 \end{Bmatrix} O_2 + 2\,Aq \\[2mm] NaO, \quad 2\,SO_2, C_{14} \begin{Bmatrix} H_5 \\ NO_4 \end{Bmatrix} O_2 + 2\,Aq \end{cases}$$

Hydride of salicyl . .	$KO,$	$2\,SO_2, C_{14}\ \ H_6\ \ \ O_4 + \ \ Aq$
Hydride of anisyl . . .	$NaO,$	$2\,SO_2, C_{16}\ \ H_8\ \ \ O_4 + \ \ Aq$
Hydride of cuminyl . .	$NaO,$	$2\,SO_2, C_{20}\ \ H_{12}\ \ O_2 + 3\,Aq$
Œnanthaldehyde . . .	$NaO,$	$2\,SO_2, C_{14}\ \ H_{14}\ \ O_2 + 3\,Aq$
Capraldehyde	$NH_4O,$	$2\,SO_2, C_{20}\ \ H_{20}\ \ O_2 + 3\,Aq.$

PROCEEDINGS

MEETINGS OF THE CHEMICAL SOCIETY.

November, 1, 1852.

PROFESSOR DAUBENY, President, in the Chair.

John William Perkins, Esq., and Joseph Török, Esq., of Paris, were duly elected Fellows of the Society.

Robert Murray, Esq., was duly elected an Associate of the Society.

The following donations were announced :

"Smithsonian Contributions to Knowledge, Vols. III. and IV."

"Report of Commissioners of Patents for 1850: Part 1. Arts and Manufactures; Part 2. Agriculture."

"Report to the Navy Department of the United States on American Coals."

"Report of the Secretary of War on the Geology and Topography of California."

"Letter from the Secretary of the Treasury on Hydrometrical Tables, &c."

"Fifth Annual Report of the Board of Regents of the Smithsonian Institution for 1850."

"On recent improvements in the Chemical Arts, by Booth and Morfit."

"Directions for collecting, preserving, and transporting Specimens of Natural History."

"The American Patent Laws."

"American Zoological, Botanical, and Geological Bibliography for 1851."

"Abstract of the Seventh American Census:"

From the Smithsonian Institution.

"Report of the Jury of the Great Exhibition on Miscellaneous Manufactures:" from the Reporters.

"Transactions of the Royal Society of Edinburgh, Vol. XX., Part 3., for 1851-52."

"Proceedings of the Royal Society of Edinburgh:" from the Royal Society of Edinburgh.

"The Quarterly Journal of the Geological Society for August, 1852:" from the Geological Society.

"The American Journal of Science and Arts:" from the Editors.

"Phillips's Elementary Introduction to Mineralogy, by Brooke and Miller:" from the Editors.

The following Resolution of the Council having been read at three meetings of the Society, was submitted to a ballot, and affirmed unanimously:

"That it be recommended to the Society that the following names be removed from the list of Fellows: Dr. R. H. Brett, Christopher Binks, W. Sands Cox, Isaiah Deck, Stanislaus Desussex, Thomas Griffiths, Thomas Hawkesley, Andrew P. Halliday, Charles J. Hodgson, George W. Mowbray, George Southby, Dr. Wilton Turner, John Turner."

The following papers were read:

1. "On the Valuation of Indigo:" by Dr. Frederick Penny.

2. "Note on the presence of Alumina in Urine:" by Lionel S. Beale, M.B.

3. "Note on the reaction of Glycocoll with Potash:" by Professor Horsford: communicated by Dr. Hofmann.

Mr. G. H. Makins exhibited and explained his improved Assay Balance.

November 15, 1852.

ROBERT PORRETT, Esq., Treasurer, in the Chair.

George Hamilton, Esq., of Liverpool, and Stephen Darby, Esq., of Leadenhall Street, were duly elected Fellows of the Society.

A specimen of leaden bullets, in a highly oxidized state, taken from a cast-iron shell, in which they had been enclosed for fifty years, was presented to the Society by Mr. F. A. Abel.

The following papers were read :

1. "On the Constitution of Stearine :" by Patrick Duffy.
2. "On the Compounds of several essential Oils with the Alkaline Bisulphites :" by C. Bertagnini, communicated by Dr. Hofmann.

December 6, 1852.

ROBERT WARINGTON, Esq., Vice-President, in the Chair.

Dr. John Smith, of Sydney, was duly elected a Fellow of the Society.

The following donations were announced :

"On the Mechanical Equivalent of Heat, by J. P. Joule, F.C.S."
"On the Air Engine, by the same."
"Heat disengaged in Chemical Combinations, by the same."
"On the Limit to the Magnetizability of Iron, by the same."
"On a powerful Electro-magnet, by the same."
"On the economical production of Mechanical Effects from Chemical Forces, by the same :" from the Author.
"Report of the Jury of the Great Exhibition on Philosophical Instruments, and processes depending upon their use :" from the Reporter.
"Second Report of the Commissioners of the Exhibition of 1851 :" 2 copies, from Dr. Lyon Playfair.

"Lecture on Industrial Instruction on the Continent, by Dr. Lyon Playfair:" from the Author.

"Subjects for Premiums offered by the Society of Arts:" from the Society of Arts.

The following papers were read:

1. "On some new Compounds of Tellurethyl:" by Professor Wöhler, communicated by Dr. Hofmann.

2. "Analytical Notes: I. On the Action of Caustic Potassa on the Phosphates; II. On the behaviour of some Oxides with Caustic Potassa in the presence of Sesquioxide of Chromium:" by A. B. Northcote and A. H. Church.

December 20, 1852.

Dr. Daubeny, President in the Chair.

Thomas William Keates, Esq., was duly elected a Fellow of the Society.

A paper was read:

"On the law of Electrolysis:" by Professor H. Buff.

Mr. Brodie made a verbal communication on the "Construction of Chemical Formulæ."

TITLES OF CHEMICAL PAPERS

IN

BRITISH AND FOREIGN JOURNALS,

PUBLISHED IN THE YEAR 1852.

A.

Acetone.—On the comportment of acetone with quick-lime: by *C. Völckel*. Ann. Ch. Pharm. lxxxii, 63.

Acid.—Note on a new acid extracted from the mother-liquor of fulminate of mercury: by *S. Cloez*. Compt. rend. xxxiv, 364.

— — On the acid of unripe grapes: by *H. Schwartz*. Ann. Ch. Pharm. lxxxiv, 82.

—— On a peculiar acid separated in the parenchyma of the lungs: by *F. Verdeil*. Ann. Ch. Pharm. lxxxi, 334.

    Acetic.—On the preparation of pure acetic acid from brandy-vinegar: by *C. Völckel*. Ann. Ch. Pharm. lxxxii, 60; Chem. Soc. Qu. J. v, 278.

    ..   .. On the manufacture of vinegar: by *Profs. Graham, Hofmann* and *Playfair*. Pharm. J. Trans. xii, 293.

    ..   .. On the preparation of pure acetic acid from wood-vinegar: by *C. Völckel*. Ann. Ch. Pharm. lxxxii, 49; Chem. Soc. Qu. J. v, 274.

    ..   .. Improvement in the quick process for manufacturing vinegar: by *A. Wimmer*. Pharm. J. Trans. xi, 578.

    ..   .. On the action of a red heat upon alcohol and acetic acid: by *M. Berthelot*. Ann. Ch. Pharm. lxxxi, 108.

    Antimonic.—On the salts of antimonic acid: by *L. Heffter*. Berl. Monatsbericht, 1852, 344; Phil. Mag. [4] iv, 399; Pogg. Ann. lxxxvi, 418.

    Arsenious.—On the combination of arsenious acid with albumen: by *Mr. Herapath*. J. Pharm. [3] xxi, 35.

    Aspartic.—On aspartic and malic acid: by *L. Pasteur*. Ann. Ch. Pharm. lxxxii, 324; Ann. Ch. Phys. [3] xxxiv, 30; *abstr.* Chem. Soc. Qu. J. v, 62.

    ..   .. Report on Pasteur's experiments on aspartic and malic acid: by *M. Biot*. Phil. Mag. [4] iv, 275.

    ..   .. On aspartic acid: by *V. Dessaignes*. Ann. Ch. Pharm. lxxxiii, 83.

    Benzoic.—On the conversion of salicylous acid into monochlorinated benzoic acid: by *L. Chiozza*. Ann. Ch. Pharm. lxxxiii, 317; Compt. rend. xxxiv, 850; Ann. Ch. Phys. [3] xxxvi, 102.

    ..   .. On the preparation of benzoic acid by means of superheated steam: by *E. A. Scharling*. Pharm. J. Trans. xi, 469.

Acid, Benzoaric.—On benzoaric acid, as a supplement to the memoir on urous acid: by *A. Göbel.* Ann. Ch. Pharm. lxxxiii, 280.

Boracic.—On the compounds of boracic acid and water with lime: by *H. Rose.* Pogg. Ann. lxxxvi, 561; lxxxvii, 1.

    ..   .. On the action of water on boracic acid and its salts: by *H. Rose.* Pogg. Ann. lxxxvi, 465.

Camphomethylic.—On camphomethylic acid: by *A. Loir.* J. Pharm. [3] xxii, 288; Compt. rend. xxxv, 328; Chem. Gaz. 1852, 469.

Capric.—On the occurrence of capric and caprylic acids in some fusel-oils: by *T. Rowney.* Chem. Soc. Qu. J. v, 22.

Carbonic.—Apparatus for the determination of carbonic acid; by *Max Schaffner.* Ann. Ch. Pharm. lxxxii, 335; Phil. Mag. [4] iv, 317.

    ..   .. General remarks on the action of water on carbonic acid and the carbonates: by *H. Rose.* Pogg. Ann. lxxxvi, 99, 279; Ber. d. Akad. d. Wissensch. zu Berlin, 1852, 209; Chem. Gaz. 1852, 318.

    ..   .. On the compounds of the oxides of cadmium and silver with carbonic acid: by *H. Rose.* Pogg. Ann. lxxxv, 302; Chem. Gaz. 1852, 181.

    ..   .. Compounds of carbonic acid and water with sesquioxide of cobalt: by *H. Rose.* Pogg. Ann. lxxxiv, 547.

    ..   .. On the combinations of carbonic acid and water with the oxides of cobalt and nickel: by *H. Rose.* Chem. Gaz 1852, 139.

    ..   .. On the compounds of carbonic acid with oxide of copper: by *H. Rose.* Chem. Gaz. 1852, 28.

    ..   .. On the compounds of carbonic acid and water with oxide of zinc: by *H. Rose.* Pogg. Ann. lxxxv, 107.

    ..   .. On the quantity of carbonic acid in the higher regions of the atmosphere: by *A. Schlagintweit.* Pogg. Ann. lxxxvii, 293.

Chromic.—On the double salt of chromate of potash and cyanide of mercury: by *C. Rammelsberg.* Pogg. Ann. lxxxv, 145.

Citraconic.—On certain products of the action of nitric acid on citraconic acid: by *S. Baup.* Ann. Ch. Pharm. lxxxi, 96.

Citric.—On the constitution of citric acid: by *L. Pebal.* Ann. Ch. Pharm. lxxxii, 78; Chem. Gaz. 1852, 318; *abstr.* Ann. Ch. Phys. [3] xxxv, 469; Chem. Soc. Qu. J. v, 284.

    ..   .. On the decomposition of citrate of lime in contact with putrefying curd: by *H. How.* Chem. Soc. Qu. J. v, 1.

    ..   .. On the occurrence of citric acid in *Richardsonia scabra*: by *Rochleder* and *Willigk.* Chem. Gaz. 1852, 43.

Crenic.—On the existence of organic matter in stalactites and stalagmites, forming crystallized and amorphous crenate of lime: by *D. A Wells.* Sill. Am. J. [2] xiii, 11; Chem. Gaz. 1852, 72.

Gallic.—On gallic acid fermentation: by *M. Robiquet.* Chem. Gaz. 1852, 297.

Hippuric.—Examination of certain products derived from hippuric acid: by *N. Socoloff* and *A. Strecker.* Ann. Ch. Pharm. lxxx, 17; Chem. Soc. Qu. J. v, 71.

    ..   .. On a new method of obtaining hippuric acid in considerable quantity without evaporation of the urine, and on some of its products of decomposition: by *E. Riley.* Chem. Soc. Qu. J. v, 97.

Acid, Hydrobromic.—On gas-batteries, and on the preparation of hydro-
bromic and hydriodic acids by the galvanic method: by *G. Osann.*
Phil. Mag. [4] iii, 317.

Malic.—Malic acid contained in *Hippophaë rhamnoides*: by *Prof. Erdmann.*
J. pr. Chem. lv, 191 ; Chem. Gaz. 1852, 253.

.. .. On aspartic and malic acid: by *L. Pasteur.* Ann. Ch. Phys.
[3] xxxiv, 30; Ann. Ch. Pharm. lxxxii, 324.

.. .. Report on Pasteur's observations on aspartic and malic acids :
by *M. Biot.* Phil. Mag. [4] iv, 275.

Meconic.—On meconic acid and some of its derivatives: by *H. How.* Ed.
Phil. Trans. xx, pt. 3, 401 ; Ann. Ch. Pharm. lxxxiii, 350; Chem.
Gaz. 1852, 301 ; *abstr.* Proc. Roy. Soc. Ed. 1851-2, 99.

Mellitic.—On some new salts of mellitic acid : by *C. Karmrodt.* Ann.
Ch. Pharm. lxxxi, 164.

Metacetonic.—On Dr. Keller's supposed formation of metacetonic acid
from flour and leather : by *R. W. Forster.* Chem. Soc. Qu J. v, 27.

Molybdic.—Process of obtaining molybdic acid from native molybdate of
lead : by *Chr. Elbers.* Ann. Ch. Pharm. lxxxiii, 215.

Nitric.—On the action of nitric acid on various vegetables, with a more
particular reference to *Spartium scoparium* : by *John Stenhouse.* Phil.
Trans. 1851, ii, 413.

.. .. On the formation of nitric acid : by *H. Bence Jones.* Ann. Ch.
Pharm. lxxxii, 368.

Nitrocinnamic.—On the action of sulphide of ammonium on nitrocin-
namic acid: by *L. Chiozza.* Ann. Ch. Pharm. lxxxiii, 117 ; Compt.
rend. xxxiv, 598.

Nitrotartaric.—On two new acids resulting from the action of nitrotar-
taric acid : by *M. Dessaignes.* Compt. rend. xxxiv, 731; Chem. Gaz.
1852, 312.

.. .. On nitrotartaric acid, and on a new acid derived therefrom : by
V. Dessaignes. Ann. Ch. Pharm. lxxxii, 362.

Nitrous.—On nitrous acid: by *M. Fritzsche.* J. pr. Chem. liii, 86 ;
J. Pharm. [3] xxi, 229.

.. . On nitrous acid and nitrosulphuric acid : by *M. Guinon.* Ann.
Ch. Phys. [3] xxxv, 144.

Œnanthic.—On œnanthic ether and œnanthic acid : by *W. Delffs.* Pogg.
Ann. lxxxiv, 505 ; Chem. Soc. Qu. J. v, 279.

Oxalic. On the manufacture of oxalic acid : Chem. Gaz. 1852, 112 ;
Pharm. J. Trans. xi, 407.

.. .. Improvements in the chemical preparation of the raw materials
used in the manufacture of paper, and in obtaining oxalic acid. Pharm.
J. Trans. xii, 258.

Oxysulphocarbonic.—On certain decomposition-products of bioxysul-
phocarbonate of ethyl, and on the spontaneous decomposition of
chemical compounds : by *H. Debus.* Ann. Ch. Pharm. lxxxii, 253.

Pelargonic.—On a compound of pelargonic acid with nitric oxide : by
L. Chiozza. Compt. rend. xxxv, 797.

Periodic.—On periodic acid and the periodates : by *M. Langlois.* Ann.
Ch. Phys. [3] xxxiv, 257 ; Ann. Ch. Pharm. lxxxiii, 153.

Acid, Phosphoric.—New method of separating phosphoric acid from metallic oxides: by *A. Reynoso.* Ann. Ch. Phys. [3] xxxiv, 301.

.. .. On the determination of phosphoric acid by molybdate of ammonia: by *W. J. Craw.* Sill. Am. J. [2] xiii, 393; Chem. Gaz. 1852, 216.

.. .. Phosphoric acid in normal human urine: by *D. Breed.* Sill. Am. J. [2] xiii, 224.

.. .. On the application of molybdic acid to the determination of phosphoric acid: by *M. Sonnenschein.* J. pr. Chem. liii, 339; Chem. Gaz. 1852, 388.

Phycic.—On phycic acid, a new acid obtained from the *Protococcus vulgaris*: by *A. Lamy.* Ann. Ch. Phys. [3] xxxv, 129.

Picric.—On picric acid considered as a yellow colouring matter: by *M. Girardin.* J. Pharm. [3] xxi, 30; Pharm. J. Trans. xi, 573.

Pyromeconic.—On some salts and products of decomposition of pyromeconic acid: by *J. F. Brown.* Phil. Mag. [4] iv, 161; Proc. Roy. Soc. Ed. 1851-2, 117; Ann. Ch. Pharm. lxxxiv, 32.

Rhodanhydric.—On the occurrence of rhodanhydric acid in a sample of commercial ammonia: by *M. Mazade.* Compt. rend. xxxv, 803.

Salicylic.—New formation of salicylic acid: by *H. Gerland.* Chem. Soc. Qu. J. v, 133.

.. .. On the transformation of salicylic acid into monochlorinated benzoic acid: by *L. Chiozza.* Ann. Ch. Phys. [3] xxxvi, 102; Ann. Ch. Pharm. lxxxiii, 317: Compt. rend. xxxiv, 850; Chem. Gaz. 1852, 319.

Silicic.—On the solubility and hydrated condition of silicic acid: by *J. Fuchs.* Ann. Ch. Pharm. lxxxii, 119.

Sulphuric.—Products of decomposition obtained by treating feathers, hedgehog's bristles, hairs, globulin, hæmatin, and the wing-cases of cockchafers with dilute sulphuric acid: by *A. C. Loyer* and *Köller.* Ann. Ch. Pharm. lxxxiii, 332.

.. .. Observations on the formation of sulphuric acid from sulphurous acid and oxygen gas. Ann. Ch. Pharm. lxxxi, 255.

.. .. On a new compound of the highest chloride of sulphur with sulphuric acid: by *H. Rose.* Pogg. Ann. lxxxv, 510.

.. .. Researches on the compounds of sulphuric acid with organic substances: by *Gerhardt* and *Chancel.* Compt. rend. xxxv, 696.

.. .. New mode of estimating sulphuric acid by means of graduated solutions: by *H. Schwartz.* Ann. Ch. Pharm. lxxxiv, 84.

Stearic.—On the detection and determination of stearic acid in bees'-wax: by *M. Overbeck.* J. Pharm. [3] xxi, 39.

Tannic.—On the tannic acids, and a new class of nitrogenous derivatives of the tannic acid series: by *A.* and *W. Knop.* Chem. Pharm. Centr. xxiii, 417; Chem. Gaz. 1852, 338.

.. .. On the constitution of tannic acid: by *A. Strecker.* Ann. Ch. Pharm. lxxxi, 247; Chem. Soc. Qu. J. v, 102; J. Pharm. [3] xxii, 292.

Tartaric.—On the nature and preparation of soluble cream of tartar: by *E. Robiquet.* J. Pharm. [3] xxi, 183.

.. .. On the mode of testing soluble cream of tartar: by *M. Lahens.* J. Pharm. 3 xxi, 110.

Acid, Tartaric.—On the modifications of tartaric acid produced by heat : by
    A. Laurent. Compt. rend. xxxv, 742.

  Ulmic.—On the absorption of soluble ulmates by plants : by *J. Malaguti.*
    Ann. Ch. Phys. [3] xxxiv, 140.

  Uroxanic.—Correction with regard to uroxanic acid : by *Prof. Städeler.*
    Ann. Ch. Pharm. lxxx, 119.

  Valerianic.—On anhydrous valerianic acid : by *L. Chiozza.* Compt.
    rend. xxxv, 568.

Acids.—On the action of acids, heat, and the chlorine-compounds of the alkali
    and earth-metals on oil of turpentine, hydrate of turpentine, sugar and
    alcohol : by *M. Berthelot.* Ann. Ch. Pharm. lxxxiii, 104.

—— Estimation of the quantities of free acids in the juices of fruit : by
    M. Græger. Chem. Gaz. 1852, 226.

—— On the direct formation of hydracids by means of porous bodies : by
    B. Corenwinder. Ann. Ch Phys. [3] xxxiv, 77.

  Fatty.—On the fatty acid of the *Cocculus indicus* : by *W. Crowder.* Phil.
    Mag. [4] iv, 21,

    ..   .. Preparation of pure fatty acids for the manufacture of candles.
    Pharm. J. Trans. xii, 137, 138.

  Organic.—Researches on the anhydrous organic acids : by *C. Gerhardt.*
    Chem. Soc. Qu. J. v, 127, 226 ; Ann. Ch. Pharm. lxxxii, 127 ; lxxxiii,
    112 ; Compt. rend. xxxiv, 755, 902.

    ..   .. On anhydrous organic acids : by *L. Chiozza.* Ann. Ch. Pharm.
    lxxxiv, 106.

Affinity.—On the relation between the density of chemical compounds and
    their solubility in water, together with a theory of elective affinity
    thence deduced : by *P. Kremers* (conclusion). Pogg. Ann. lxxxv, 246.

Agarics.—Poisonous agarics ; method of removing the poisonous principle.
    J. Pharm. [3] xxi, 155.

Air.—Researches on the composition of atmospheric air : by *V. Regnault.*
    Compt. rend. xxxiv, 863.

—— On the extraction of oxygen gas from atmospheric air : by *M. Boussingault.*
    Ann. Ch. Phys. [3] xxxv, 5 ; *abstr.* Compt. rend. xxx, 261 and 821 ;
    Chem. Soc. Qu. J. v, 269.

—— On the composition of the air enclosed in vegetable mould : by *Boussing-
    ault* and *Lewy.* Compt. rend. xxxv, 765.

Air-pump.—New construction of the air-pump, by which the injurious
    spaces are completely obviated : by *E. Schöhl.* Pogg. Ann. lxxxiv, 544.

—— On a method of obtaining a perfect vacuum in the receiver of an air-
    pump : by *T. Andrews.* Phil. Mag. [4] iii, 161 ; Chem. Soc. Qu. J. v,
    189.

Albumin.—On albumin and casein : by *N. Lieberkühn.* Pogg. Ann. lxxxvi,
    117, 298.

—— On the combination of arsenious acid with albumin : by *Mr. Herapath.*
    J. Pharm. [3] xxi, 35.

—— Causes of the passage of albumin into the urine : by *E. Robin.* Compt.
    rend. xxxiii, 698.

—— On paralbumin and metalbumin : by *J. Scherer.* Ann. Ch. Pharm. lxxxii,
    135.

Alcohol.—On the action of a red heat on alcohol and acetic acid : by *M. Berthelot*. Ann. Ch. Pharm. lxxxi, 108.

—— On the dehydration of alcohol : by *A. Gorgeu*. Compt. rend. xxxiii, 690; J. Pharm. [3] xxi, 259.

—— On the action exerted by acids, by heat, and by alkaline and earthy chlorides on oil of turpentine and its hydrate, on sugar and on alcohol: by *M. Berthelot*. Compt. rend. xxxiv, 799; Ann. Ch. Pharm. lxxxiii, 107.

—— On butylic alcohol : by *A. Wurtz*. Compt. rend. xxxv, 310; Chem. Gaz. 1852, 386.

Aldehyde-ammonia.—Formation of oxalic ether and oxamide by the distillation of aldehyde-ammonia : by *C. Schmidt*. Ann. Ch Pharm. lxxxiii, 330.

Ale.—Report on the alleged adulteration of pale ales by strychnine : by *Profs. Graham* and *Hofmann*. Chem. Soc. Qu. J. v, 173; Ann. Ch Pharm. lxxxiii, 39.

Algæ.—Examination of the seaweeds of the coasts of Lower Normandy: by *J. Pierre*. Compt. rend. xxxiv, 107.

Alkalies.—Indirect method of determining magnesia and the alkalies when they occur together : by *K. List*. Ann. Ch. Pharm. lxxxi, 117.

—— Formation of the ethylic alkalies by means of chloride of ammonium : by *M. Berthelot*. Compt. rend. xxxiv, 802.

—— On the compounds of cotton with the alkalies : by *J. H. Gladstone*. Chem. Soc. Qu. J. v, 17.

Alkaloids.—On a general method of detecting organic alkaloids in cases of poisoning : by *Prof. Stas*. J. Pharm. [3] xxii, 281 ; Pharm. J. Trans. xii, 195; Chem. Gaz. 1852, 348.

—— Contribution to the chemical history of the mercury-compounds of the alkaloids : by *Fr. Hinterberger*. Ann. Ch. Pharm. lxxxii, 311.

—— On the quantity of alkaloids contained in many cinchona barks : by *E. Riegel*. Pharm. J. Trans. xii, 258.

—— On the combinations of the vegetable alkaloids with tartaric acid; by *M. Arppe*. J. pr. Chem. li, 331 ; Chem. Gaz. 1852, 9.

—— On the mercurial compounds of the alkaloids : by *Dr. Hinterberger*. Sitzungsber der Akad. der. Wissench. zu Wien. vii, Heft. 3 ; Chem. Gaz. 1852, 422, 444.

Allotropy.—On the allotropy of selenium : by *W. Hittorff*. Pogg. Ann. lxxxiv, 214 ; *abstr.* Phil. Mag. [4] iii, 546; Chem. Soc. Qu. J. v, 90.

Alloy.—Analysis of a new alloy for the plates of calico-printers : by *C. Fischer*. J. pr. Chem. lv, 192; Chem. Gaz. 1852, 279.

Alloys.—Memoir on alloys considered with relation to their chemical composition : by *A. Levol*. Ann. Ch. Phys. [3] xxxvi, 193.

—— On the position of alloys and amalgams in the thermo-electric tension-series : by *W. Rollmann*. Pogg. Ann. lxxxiv, 275.

—— On an alloy of potassium and sodium : by *R. Wagner*. J. pr. Chem. lv, 489; Ann. Ch. Phys. [3] xxxvi, 246.

—— Note on a new alloy of silver : by *G. Barruel*. Compt. rend. xxxv, 759.

Aloes.—On Socotrine aloe-juice, or liquid Socotrine aloes : by *J. Pereira*. Pharm. J. Trans. xi, 439.

Aloine.—On aloine, the crystalline cathartic principle of Barbadoes aloes : by
J. Stenhouse. Pharm. J. Trans. xi, 458 ; J. Pharm. [3] xxi, 427.

Alum.—Application of the slag of blast-furnaces to the preparation of alum,
chloride of calcium, &c. Pharm. J. Trans. xii, 259.

Alumina.—Alumina in *Lycopodium Chamæcyparissus*, and *L. clavatum*: by
A. Aderholdt. Ann. Ch. Pharm. lxxxii, 111.

—— On the preparation of sulphate of alumina : by *MM. Huria* and *Brunel.*
Bull. Soc. d'Encourag. 1852, 199 ; Chem. Gaz. 1852, 359.

'Amazon.'—Chemical report on the cause of the fire in the 'Amazon :' by
T. Graham. Chem. Soc. Qu. J. v, 534.

Amides.—On the combinations of certain amides : by *V. Dessaignes.* Ann.
Ch. Pharm. lxxxii, 231 ; Compt. rend. xxxiii, 712 ; Ann. Ch. Phys.
[3] xxxiv, 143.

Ammonia.—Easy decomposition of ammonia. New source of pure hydrogen
for the reduction of metallic oxides : by *M. Bouet-Bonfil.* Ann. Ch.
Phys. [3] xxxvi, 225 ; Compt. rend. xxxiv, 588.

—— On the oxidation of ammonia in the human body, with some remarks on
nitrification : by *H. Bence Jones.* Phil. Trans. 1851, ii, 399 ; Ann.
Ch. Phys. [3] xxxv, 176.

—— Presence of ammonia in hail : by *C. Mène.* Pogg. Ann. lxxxiv, 234.

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